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Viability of Biopolymers for Enhanced Oil Recovery

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GRAPHICAL ABSTRACT

Xanthan gum and scleroglucan are assessed as environmentally friendly enhanced oil recovery (EOR) agents. Viscometric and interfacial tension measurements show that the polysaccharides exhibit favorable viscosifying performance, robust shear tolerance, electrolyte tolerance, and moderate interactions with surfactants. Non-ionic surfactants and anionic surfactants bind to xanthan gum and transform the backbone conformation from a strong helix to a more flexible structure, reducing the viscosifying efficacy of xanthan. In contrast, non-ionic surfactants and anionic surfactants bind to scleroglucan and increase the viscosifying efficacy by non-electrostatic interactions or imparted electrostatic effects. The two polysaccharides are technically viable as viscosifying agents in typical EOR injection fluid formulations.

Keywords EOR, scleroglucan, xanthan gum

1. INTRODUCTION

Chemical enhanced oil recovery (EOR) techniques are often applied to petroleum production due to relatively simple application and reasonable incremental production costs. Chemical EOR processes use interfacial tension reduction and/or mobility ratio enhancement to mobilize oil.^[1] EOR operations are typically based on polymer flooding or alkali–surfactant–polymer flooding.^[2] The presence of surfactant reduces interfacial tension between the aqueous and hydrocarbon phases. Capillary forces

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/ldis.

are reduced, promoting oil mobilization.^[3] Recovery also improves via viscosity matching. Viscous fingering is reduced or eliminated, improving sweep efficiency. Tailored EOR injection fluids often contain water soluble polymers, such as polyacrylamides. The polymers increase aqueous phase viscosity, reducing permeability contrast. Operational risks associated with EOR flooding include polymer loss to the porous media, polymer degradation, and in some cases, loss of injectivity.

Partially hydrolyzed polyacrylamide (HPAM) is the most widely used synthetic water-soluble polymer in EOR applications.^[4] HPAM is a copolymer which consists of acrylamide and acrylic acid, and is synthesized by partial hydrolysis of polyacrylamide (PAM) or alternatively by copolymerization of sodium acrylate with acrylamide.^[4,5] The degree of hydrolysis of acrylamide monomers is typically ~30%,^[4] and the molar mass of the product is as high as 30 million Da. At low concentration, HPAM exists in solution as a flexible chain (random coil). HPAM shows favourable viscosifying performance and robust tolerance toward shear forces present during reservoir flooding. HPAM is also resistant against bacterial degradation.^[4,6] Polyacrylamide-based EOR polymers also have distinct disadvantages. As a result of repeating electrical charges along the backbone, HPAM interacts with charged species in solution. HPAM is also sensitive toward the presence of hydrocarbons and surfactants (indigenous or synthetic) in the reservoir. In addition, precipitation may occur if multivalent salts are present in the injection water.^[8] Recent R&D activities have focused on modified HPAM chemistries. Introduction of additional polymeric chemistries yields efficient EOR polymers which are suitably adapted to high-mineralization and high-temperature reservoirs.^[7,8]

From an environmental perspective, synthetic polymer usage in EOR is undesirable. After injection, HPAM either remains in the reservoir or follows the o/w dispersion out of the reservoir via a production well, requiring separation for recovery. In optimal cases, most injected HPAM is retained in the reservoir. Due to forthcoming environmental regulations, industrial processes are mandated to reduce usage and spillage of non-biodegradable polymers, which contribute strongly to bio-accumulation in the case of unintended environmental release. As a consequence, biopolymer-based EOR formulations will become more appealing in the future. Nanocellulose and various polysaccharides are environmentally friendly candidates which may be able to fully or partially replace HPAM in future chemical EOR operations.

Essential physical characteristics of biopolymer candidates for EOR include high viscosifying efficacy at low additive concentration and low sensitivity toward shear degradation. In order to effectively impart high solution viscosity, molar mass should be large and the biopolymer should be water-soluble.^[9–11] According to Standnes and Skjevrak,^[12] 92% of reported polymer flooding projects

utilize HPAM as viscosifying agents, with the remaining projects using biopolymers or hydrophobic associate polymers. Xanthan gum is the only biopolymer which has been applied commercially in petroleum reservoirs.^[4,12] Xanthan gum is a rigid polysaccharide and does not degrade by typical shear forces present in petroleum reservoirs. Xanthan gum is relatively insensitive to high electrolyte concentrations and does not precipitate in the presence of divalent ions.^[10] Another biopolymer, Schizophyllan, is currently undergoing field testing for EOR. Schizophyllan is produced by the common fungus *Schizophyllum commune*. It is claimed that Schizophyllan remains effective at high thermal and salinity conditions.^[13,14]

In order to suitably replace synthetic EOR polymers such as HPAM, biopolymer candidates should exhibit high thermal tolerance, high salinity tolerance, high mechanical and shear stability, favourable rheological and adsorption properties, and a high viscosifying efficacy. In the current investigation, viscous and interfacial tension properties are investigated to assess the suitability of biopolymer formulations for EOR. Three polysaccharide-based biopolymers with known viscosifying properties are investigated: starch, xanthan gum, and scleroglucan. Xanthan gum and scleroglucan are known to show high tolerance toward salinity as well as high tolerance toward water hardness. Both polymers exist in a helical structure in saline solution; xanthan gum exists as a negatively charged double helix; scleroglucan forms an uncharged triple helix. Rigid helical structures are characterized by high persistence lengths, and also prevent the formation of surfactant–polymer complexes due to effective shielding of hydrophobic moieties of the polysaccharide.^[15] Disadvantages of biopolymer application for EOR include a high economic cost as well as ease of biodegradation. Polymeric residence time distributions are reservoir-specific. In some cases, substantial biodegradation occurs only after EOR operations are complete, and biodegradability may be advantageous. In other cases, effective biocides may be required in the injection fluid formulation in order to prevent microbial degradation.^[6] These challenges must be overcome for biopolymers to successfully replace HPAM. However, these operational challenges lie beyond the scope of the current report, where the aim is to assess the viscosifying performance of promising biopolymer candidates in realistic EOR formulations and to reveal biopolymer–surfactant interactions. Tolerance toward electrolyte, mechanical shear, and surfactants is investigated. Economic aspects are not considered in the current study.

2. EXPERIMENTAL SECTION

2.1. Materials

Biopolymer solutions are prepared for viscosity measurements by dissolving the respective polymer powder

in ultrapure water using magnetic stirring until a homogeneous aqueous solution is attained, or alternatively for more than 1 hour. Polymer solutions containing starch were heated for ~ 2 hours at 70°C until solution clarity was attained. For viscometric experiments performed in conjunction with surfactant and/or salt, a stock solution of biopolymer was prepared. Also, stock solutions were prepared for surface and interfacial tension experiments.

Xanthan gum, produced from *Xanthomonas campestris*, was purchased from Sigma-Aldrich (St. Louis, MO). Scleroglucan was purchased from Elicityl OligoTech (Crolles, France). Starch containing $>95\%$ amylopectin was supplied by Avebe (Veendam, the Netherlands). Dodecane was purchased from Sigma-Aldrich (St. Louis, MO) for the interfacial tension experiments. ENORDET O332, an internal olefin sulfonate with a $\text{C}_{15}\text{--}\text{C}_{18}$ carbon number range, was supplied by Shell Chemicals (Moerdijk, the Netherlands).^[16] The active matter (AM) of the surfactant is 32%. Both pure and diluted surfactants were used; dilution was performed with ultrapure water. Tween[®] 80, a non-ionic surfactant, was purchased from Sigma-Aldrich (St. Louis, MO).

2.2. Viscometry

Viscometric experiments were conducted using a Physica MCR 301 (Anton Paar, Austria) rotational rheometer equipped with concentric cylinder geometry CC27 (ISO3219). The radius of the measuring bob is 13.33 mm and the radius of the measuring cup is 14.46 mm. Samples were measured at specified temperatures of 25°C , 50°C , and 75°C ($\pm 0.01^\circ\text{C}$); thermal regulation is provided by a Peltier element. Prior to data collection, each sample was pre-heated at the specified temperature for 10 minutes at quiescent conditions. The sample was then pre-sheared at the identical specified temperature for 6 minutes at 1000 s^{-1} in order to confirm tolerance toward high mechanical shear forces. Shear stress measurements were obtained by reverse ramping the prescribed shear rate from 1000 s^{-1} to 0.1 s^{-1} . Reverse ramping was selected in order to minimize transient hysteretic artefacts.

2.3. Interfacial Tension

Surface tension and interfacial tension of polymer solutions were measured using a Sigma 703 ring tensiometer at room temperature conditions ($20 \pm 1^\circ\text{C}$). The tensiometer was calibrated with ultrapure water. In order to minimize undesired artefacts, the platinum ring was pre-cleaned with detergent and water and further pre-cleaned by flaming. Glassware was pre-cleaned with water, acetone, and toluene and finally rinsed with pure water. A small beaker containing 20 mL of polymer solution was used for measurements. For interfacial tension measurements, 20 mL of dodecane was added indirectly to the surface. Surface tension values were measured until the observed reduction in surface tension was less than 1 mN/m in 1 hour.

3. RESULTS AND DISCUSSION

3.1. Biopolymer Solution Viscosities

Distinct shear thinning of xanthan gum, scleroglucan and starch solutions is shown in Figure 1. Observed viscosity minima in the vicinity of 800 s^{-1} for 1500 ppm xanthan gum and in the vicinity of 600 s^{-1} for 2500 ppm scleroglucan indicate the onset on inertially driven secondary flows (Taylor vortices), and do not indicate shear-thickening. The onset of secondary flows for 10,000 ppm starch occurs at shear rates higher than 1000 s^{-1} (due to higher viscosity and reduced Taylor number). Favorable viscosifying performance of xanthan gum and scleroglucan at moderate shear rates derives from rigid double- and triple-helical conformations, respectively, characterized by long persistence lengths. High persistence lengths provide large random coil volumes and extensive coil overlap, facilitating intermolecular interactions and entanglement at low overall polymer content. In the literature, xanthan gum solution viscosity has been modeled as a power law function at moderate-to-high shear rates.^[17–19] At low shear rates, xanthan gum solutions and scleroglucan solutions show Newtonian behavior. Solution viscosities measured at a shear rate of 10 s^{-1} are shown in Table 1 for various biopolymer concentrations and temperatures. Observed nonlinear increases in viscosity at increasing xanthan gum concentrations are interpreted as a consequence of intermolecular interactions or entanglements. Physical interactions increase apparent molecular weight and associated effective macromolecular dimensions.^[20] On the other hand, at increasing shear rate, an opposite effect is observed; apparent viscosity decreases. This process is attributed to destruction of molecular aggregates

FIG. 1. Biopolymer solution viscosities as a function of shear rate at 25°C .

TABLE 1
Viscosities (mPa · s) of xanthan gum, scleroglucan,
and starch aqueous solutions at various
concentrations and a shear rate of 10 s^{-1}

Xanthan gum concentration (ppm)	25°C	50°C	75°C
200	9.65	6.74	4.59
1500	80.53	60.45	45.58
2000	121.10	90.67	69.04
2500	163.52	120.43	88.37
5000	468.83	363.89	249.01
Scleroglucan concentration (ppm)	25°C	50°C	75°C
200	2.66	1.71	1.35
1500	13.56	10.12	9.23
2000	34.76	28.64	25.89
2500	70.64	61.46	55.63
5000	152.84	169.15	183.29
Starch concentration (ppm)	25°C	50°C	75°C
200	1.02	0.98	1.03
1500	1.67	1.28	1.40
2000	4.68	2.11	1.77
5000	10.84	6.74	4.68
10,000	36.09	29.16	16.13
20,000	66.41	43.74	29.16

and orientation of polymer molecules in the flow direction, reducing the overall flow resistance by several complex sub-mechanisms.^[18] Scleroglucan solutions show high viscosity at low concentration, attributable to high molecular weight and structural chain rigidity.^[21] For high amylopectin-content starch solutions, the literature indicates viscosity enhancement at increasing starch concentration, attributable to intermolecular interactions such as entanglements between branched molecules.^[22]

At low aqueous concentrations, the selected biopolymers show thermal sensitivity, which is partially attributable to reduced chain stiffness at increasing temperature conditions.^[21,23] The viscosity of xanthan gum is distinctly thermally dependent, deriving from a thermal transition from a double helical conformation at low temperatures to a disordered coil structure at higher temperatures.^[17] Scleroglucan, on the other hand, is a semi-rigid chain composed of three helix strands which are stabilized by hydrogen bonds. The stabilized triple helix structure transforms to a single-chain random-coil at temperatures above 135°C, which is the effective melting temperature of triple

helices into single chains.^[24] In the current report, rheological behavior is assessed at a maximum temperature of 75°C, which is significantly lower than the associated melting temperature of the triple helix. Most conventional petroleum reservoirs are colder than 135°C, assuring relevance of the triple helix state to EOR processes. Viscosity trends shown in the current report for scleroglucan are attributable to changes in chain stiffness, conformations, intermolecular association, and entanglements.

A distinct viscosity increase is evident for 5000 ppm scleroglucan at increasing temperatures, as shown in Table 1. Similar trends for scleroglucan have previously been observed in the semi-dilute concentration regime.^[25] The demonstrated viscosity increase is attributable to a larger degree of intermolecular association or to a larger degree of swelling.^[25] Temperature dependent entropic effects are also likely responsible for the increasing viscosity of 5000 ppm scleroglucan at increasing temperatures.

At biopolymer concentrations greater than the relevant gelation threshold, plastic rheology dominates instead of shear-thinning rheology. In the literature, a scleroglucan gelation threshold has been previously established in the vicinity of 2000 ppm to 3000 ppm.^[25] From an EOR processing perspective, it is imperative to avoid plastic rheology in continuous injection fluids for petroleum reservoirs. Very small length scales associated with pore throats generate effective fluid immobilization and/or severe flow diversion (at macro- and micro-length scales) when plastic fluids are injected, due to an inverse length-scale dependence of pressure gradient contributions from yield stresses. Even weak plastic fluids are synergistically immobilized in porous media, resulting in inhomogeneous reservoir sweep and artificially high pressure gradients. Scleroglucan contents approaching 5000 ppm may prove counterproductive in EOR. In targeted water shut-off applications, on the other hand, fluid immobilization and diversion of flow are properly exploited, and plastic rheology of in-situ gelled fluids is highly advantageous.

In order to assure relevance for conventional EOR, measured biopolymer solution viscosities should be $\sim 80 \text{ mPa} \cdot \text{s}$ at a shear rate of 10 s^{-1} and standard temperature and pressure conditions. Table 1 shows that $80 \text{ mPa} \cdot \text{s}$ viscosity is unachievable at starch concentrations below 2 wt.%. At respective concentrations of 1500 ppm and 2900 ppm, xanthan gum and scleroglucan impart solution viscosities of $\sim 80 \text{ mPa} \cdot \text{s}$ at 10 s^{-1} . Therefore, further experiments were performed with xanthan gum at 1500 ppm and with scleroglucan at 2900 ppm. Due to poor viscosifying efficacy, no further experiments were performed with starch.

3.2. Biopolymer-Electrolyte Interactions

Figure 2 shows the effect of brine (3.5 wt.% NaCl) on the viscosity of 1500 ppm xanthan gum and 2900 ppm

FIG. 2. Effect of salinity on biopolymer solution viscosity at 25°C.

scleroglucan at 25°C. Xanthan gum viscosity decreases in the presence of salt, due to standard electrostatic screening (random coil retraction) as well as changes in the conformational state of side chains and backbone, as inferred from potentiometric titrations and viscometry data.^[20] When electrostatic interactions are screened by electrolyte, xanthan gum exists in an ordered helical conformational state in which side chains are associated with the backbone via strong hydrogen bonding interactions. In the absence of electrolyte, side chains extend away from the backbone and the backbone exists in an elongated state due to unscreened intra-molecular electrostatic repulsive forces, despite a smaller inherent persistence length associated with the weaker and more disordered backbone. Sidechain extension and random coil expansion, in the absence of salt, effectively increase the biopolymer hydrodynamic volume, entanglements, and solution viscosity.^[20] Conversely, sidechain-backbone association and random coil retraction in the presence of salt is consistent with reduced hydrodynamic volume, reduced intermolecular entanglement, and lower viscosity. (Viscosity reduction of HPAM by salt-driven retraction is well known and accounted for in product formulations.) The viscosity offset deriving from the presence of electrolyte is robust and is partially retained at high shear rates in which xanthan gum adopts an overall elongated chain conformation as a result of shear alignment. The partially retained viscosity offset confirms that the electrolyte-driven sidechain dissociation event is sustained at the elongated chain conformation, in accordance with the increased hydrodynamic volume of the dissociated state of the side chains. Scleroglucan, on the other hand, shows high stability toward brine. No viscosity reduction is observed in the presence of salt. At low shear rates, a small viscosity increase is evident, consistent with sparse

intra-chain or inter-chain repulsive interactions which become screened under the presence of electrolyte.

3.3. Xanthan Gum Interactions

Anionic or non-ionic surfactants are added to biopolymer solutions to assess viability for EOR. At small and moderate surfactant concentrations, observed viscosity changes are primarily attributable to intermolecular interactions between the biopolymer and the surfactant. Depending on specific charge characteristics as well as relative hydrophobicity, various types of interactions are possible, ranging from a complete absence of surfactant binding (only additive viscous contributions) to formation of surfactant-polymer complexes or aggregates.^[19]

Viscosity is measured as a function of shear rate at various salt and surfactant concentrations. At 25°C, the viscosity of xanthan gum is quantitatively similar for molar equivalencies of salt or anionic surfactant (result not shown), independent of concentration, indicating that solely charge screening surfactant interactions are relevant at 25°C, and also confirming that small-magnitude hydrodynamic volume effects specifically related to polymer-surfactant binding are negligible and do not influence measured viscosity curves at low surfactant contents. Beyond conformational changes resulting from increased ionic strength (associated with the charged surfactant), additional structural transition events are not induced by anionic surfactant at 25°C. Viscosity is reduced by only electrostatic screening. At 50°C, on the other hand, anionic surfactant does reduce the viscosity of xanthan gum in a non-electrostatic capacity. Figure 3 depicts interactions between xanthan gum and surfactants or salt at 50°C.

FIG. 3. Effect of low salt or surfactant content on xanthan gum solution viscosity at 50°C.

Observed viscosity reductions, attributable to polymer chain retraction (reduced chain entanglement), are largest with non-ionic surfactant, indicating strong binding interaction of non-ionic surfactant with xanthan. At high shearing rates in which polymer chains naturally adopt extended conformations due to shear alignment, the retraction mechanism becomes inapplicable, and the viscosity is largely independent of surfactant concentration, as confirmed by convergence of viscosity curves in Figure 3 at the high shear rate regime. The result can be understood as a consequence of surfactant acting primarily on the overall conformational state of the polymer (persistence length) at 50°C, and not on the association state of side chains. Side chain dissociation events would inevitably be strongly reflected at high shear rates as well as at low shear rates, due to inviolable hydrodynamic volume effects. A unifying hypothesis is that the state of the side chains is already established as an equilibrium distribution between associated and freely extended states, and does not respond to small changes in electrolyte or surfactant concentration. Instead, surfactants act on the persistence length of xanthan gum, which is reflected in viscometry only at low and moderate shear rates in which the polymer adopts an un-extended random coil-like structure.

Further investigation into non-electrostatic effects reveals that non-ionic surfactant is able to induce structural transition events in xanthan at 25°C. No concentration dependence was evident in the observed viscosity reduction of xanthan gum by non-ionic surfactant at 25°C. Figure 4 shows overlapping xanthan gum viscosities at various non-ionic surfactant contents, indicating that the concentration

FIG. 4. Effect of non-ionic surfactant content on xanthan gum solution viscosity at 25°C.

dependence of non-ionic surfactant activity on xanthan gum viscosity terminates at a very low concentration, portending a transition in the backbone conformation of xanthan gum in the presence of non-ionic surfactant. The transition likely involves a change from the rigid ordered double helix structure to a less ordered and less rigid backbone conformation characterized by a shorter persistence length. The weaker backbone structure effectively imparts coil retraction, reduced entanglement, and lower viscosity to the xanthan gum solution. Structural transition-driven viscosity reduction is valid only at the un-elongated polymer state, resulting in convergence of the viscosity curves shown in Figure 4 at high shear rates. The observed absence of a concentration dependence in the resultant viscosity curves (Figure 4) is a unique feature of the uncharged surfactant.

Addition of anionic surfactant effects a non-electrostatic reduction in viscosity of xanthan gum at 50°C; however, this reduction is less significant than the viscosity reduction imparted by non-ionic surfactant at 50°C (Figure 3). Addition of an equivalent amount of salt (on a molar basis) as anionic surfactant has nearly no effect on the xanthan gum solution viscosity. If only electrostatic shielding were relevant, viscosity change upon addition of salt and anionic surfactant would be quantitatively similar. The entirely dissimilar observed behaviour confirms that intermolecular interaction between xanthan gum and anionic surfactant is primarily non-electrostatic in nature, similar to the illustrated non-electrostatic interaction between xanthan gum and non-ionic surfactant.

At 75°C, observed viscosity variations are wider, but follow the same trends which were revealed at low surfactant concentrations. Absolute viscosity differences increase as surfactant concentration and temperature increase. The trend of salt displaying the smallest effect and non-ionic surfactant displaying the largest effect holds for each surfactant concentration and temperature examined, except at the highest temperature and concentration. The overall trend corroborates the conformational interpretation of polymer-surfactant interactions. Changes in xanthan gum chain conformation induced by surfactant appear to be more pronounced at higher temperatures where polymer chain segments are more susceptible to induced structural changes.

At 50°C and 75°C and a surfactant/salt concentration of 2.8 mmol/L, the non-ionic surfactant has a weaker impact on xanthan gum viscosity than the anionic surfactant, as shown in Figure 5 for the 75°C case. This phenomenon may be understood in light of a dual activity mechanism of anionic surfactant, where electrostatic as well as non-electrostatic interactions are relevant. The effect of anionic surfactant addition is therefore quantitatively similar to the effect of the simultaneous presence of salt (in an equivalent molar amount) as well as the

FIG. 5. Effect of high salt or surfactant content on xanthan gum viscosity at 75 °C.

non-electrostatic interaction imparted by the anionic surfactant. Increasing the non-ionic surfactant concentration has no effect on viscosity, although increasing anionic surfactant concentrations results in a distinct viscosity reduction. A probable interpretation of this effect is that anionic surfactant simultaneously acts as a salt and as a non-ionic surfactant. Although the effect of non-electrostatic surfactant binding to the polymer chain may level out at low concentration, the demonstrated effect of ionic strength on polymeric chain conformation implies that the anionic surfactant retains a more robust concentration dependence than the non-ionic surfactant. Finally, an interesting corroboration emerges from the data shown in Figure 5. A substantial portion of the viscosity reduction attributed to high salt and high anionic surfactant transfers to the high shear rate regime, supporting the hypothesis that large changes in ionic strength serve to alter the distribution of side chain orientations, even if effected by surfactant charge instead of NaCl. This hypothesis is corroborated by the effect of non-ionic surfactant shown in Figure 5, where a substantially smaller portion of the associated viscosity reduction translates to higher shear rates. At shear rates above $\sim 400 \text{ s}^{-1}$, the viscosity reduction activity of non-ionic surfactant is almost completely diminished, even though the non-ionic surfactant is present at a relatively high concentration (2.81 mM). Lacking electrical charges, the non-ionic surfactant is unable to influence the distribution of side chain orientations on the xanthan gum polymer in the elongated state and reduce the hydrodynamic volume. (Additional corroboration of this hypothesis is evident in Figure 7a.)

3.4. Scleroglucan Interactions

Scleroglucan is a neutral biopolymer which is not expected to show sensitivity to low electrolyte concentrations. In solution, scleroglucan chains assume rod-like triple helices which are prevented from aggregating due to D-glucosidic side groups.^[26] Figure 6 shows the viscosity at 50 °C of scleroglucan at low salt/surfactant concentrations. Viscosity increases with addition of salt or surfactant at all examined temperatures. At low added salt contents, a very small (almost negligible) viscosity increase is observable. Salt and anionic surfactants give rise to a viscosity increase at moderate concentrations.

Non-ionic surfactant exhibits the greatest activity in increasing scleroglucan solution viscosity. This observation may be explained by the fact that non-glucan molecules can become trapped within the one-dimensional hydrophobic cavity which is formed inside the (1,3)- β -D-glucans. With anionic surfactant, solution viscosity increases due to surfactant binding, and the polymer may potentially be transformed into a polyelectrolyte with a more extended conformation. However, the fact that the measured viscosity offset translates partially to the high shear rate regime provides strong evidence that the viscosity increase is at least partially non-electrostatic in nature. Scleroglucan is less thermally sensitive than xanthan gum, which is due to the fact that the melting temperature of the triple-helix structures is $\sim 135^\circ\text{C}$; thus, denaturation does not occur below $\sim 135^\circ\text{C}$, and the helix structure is retained.^[27] Trends shown in Figure 6 were observed at all concentrations and temperatures, confirming minimal electrolyte and temperature impact on scleroglucan. All measured viscosity increases for scleroglucan translate partially to

FIG. 6. Effect of low salt or surfactant concentration on scleroglucan viscosity at 50 °C.

the high shear rate regime, which is consistent with the directionality of increased hydrodynamic volume of scleroglucan with bound surfactant. Due to the magnitude of the sustained viscosity increase at low non-ionic surfactant concentrations, other non-electrostatic mechanisms in addition to hydrodynamic volume effects also likely account for the viscosity increase.

All favorable characteristics, including high thermal tolerance, high shear tolerance, and high salt tolerance, as well as increased viscosity in the presence of surfactant, collectively demonstrate that scleroglucan is a promising candidate for EOR polymer flooding. However, the influence of anionic surfactant in brine is different when comparing xanthan gum and scleroglucan (Figure 7). For xanthan gum, there is only a small effect of additional anionic surfactant at high salt content, in comparison to surfactant free brine. At high salt content (3.5 wt%), when anionic surfactant is present at concentrations below the CMC, no change in viscosity is evident in comparison to the surfactant-free solution. However, when anionic surfactant is present at concentrations above the CMC, a slight viscosity increase is observable in comparison to the surfactant-free polymer solution. For scleroglucan, on the other hand, viscosity increases with the addition of both salt and anionic surfactant, such that the presence of both salt and anionic surfactant results in an even greater viscosity increase. The significant observed viscosity increase requires the presence of anionic surfactant, but is relatively independent of the anionic surfactant concentration. The increase in viscosity is attributed to anionic surfactant binding to scleroglucan. However, because electrostatic interactions are screened at 3.5 wt.% NaCl, it is improbable that the viscosification mechanism involves electrostatic coil expansion. Instead, non-electrostatic effects are likely responsible for the viscosity increase, which is corroborated by three conditions: (1) absence of a concentration dependence of non-ionic surfactant, which is more consistent with non-electrostatic effects than with electrostatic effects, (2) the screened conditions with 3.5 wt.% NaCl, and (3) translation of a small portion of the viscosity increase to high shear rate conditions where the polymer exists in a shear aligned state. Instead, the non-electrostatic effects likely involve hydrodynamic volume effects as well as imparted inter-chain association effects, due to the implausibility of anionic surfactant increasing the stiffness of the already rigid triple-helix structure.

3.5. Interfacial Activity

The observed critical micelle concentration (CMC) of the anionic surfactant in combination with the biopolymers is higher than the observed CMC of the neat anionic surfactant, as shown in Figure 8. Scleroglucan delays the CMC the most which is attributable to binding of anionic surfactant to the backbone. Less monomer is available to

FIG. 7. Viscosity at 25°C for a) 1500 ppm xanthan gum and b) 2900 ppm scleroglucan.

reduce the surface tension, leading to higher observed CMC values. Surface tension trends are consistent with increased viscosities observed when anionic surfactant is added to scleroglucan. Xanthan gum has the caveat that bound surfactants weaken the backbone. Identical trends are observed in interfacial measurements against dodecane. CMC values of the surface and interfacial tension are shown in Table 2, and support the hypothesis that anionic surfactant binding to xanthan gum and scleroglucan is responsible for non-electrostatic changes in viscosity. The non-electrostatic portion of surfactant-driven changes to the xanthan gum viscosity do not translate to high shear

FIG. 8. a) Surface tension and b) interfacial tension of solutions at 20°C.

rates, and likely involve a transition related to the backbone structure which does not significantly impact the overall shear aligned conformational state at high shear rates conditions. On the other hand, for scleroglucan,

backbone structural transitions are not possible at temperatures below 135°C. Therefore, associated surfactant likely impacts scleroglucan via non-electrostatic association effects and hydrodynamic volume effects.

4. CONCLUSION

Biopolymers, as biodegradable substances, may serve to improve the environmental profile of chemical EOR operations, and exhibit suitable properties to replace synthetic polymer flooding agents such as HPAM. Environmental impact in the case of unintended spillage is reduced, and produced water quality will also benefit in the future from an absence of non-biodegradable polymeric substances.

Three polysaccharides were investigated using viscometric and interfacial tension measurements. Xanthan gum and scleroglucan exhibit favorable viscosifying performance in the semi-dilute regime, owing to rigid helical chain structures characterized by large persistence lengths. In addition, both xanthan gum and scleroglucan exhibit adequate tolerance toward electrolyte, especially at moderate and high shear rates where the biopolymers exist in shear-aligned states characterized by sparse inter-chain entanglements. Xanthan gum is a polyelectrolyte with side chains that may associate with the backbone under screened electrostatic conditions, resulting in marginally reduced hydrodynamic volumes as well as marginally reduced viscosities throughout the entire range of measured shear rates. Polyelectrolyte backbone retraction due to the presence of electrolyte reduces viscosity primarily at low and moderate rates of shear. At high shear rates, shear alignment artificially extends the polyelectrolyte chain, negating coil retraction effects. Scleroglucan, as a neutral polymer, is largely insensitive to electrolytes.

Biopolymer-surfactant interactions are more complex than biopolymer-electrolyte interactions. Reduced viscosities are observed for xanthan gum in the presence of surfactant, and increased scleroglucan viscosities are observed in the presence of surfactant. Observed viscosity changes are attributable to polymer-surfactant interactions which influence the secondary helical structure of the biopolymer. For xanthan gum, bound and unbound

TABLE 2
Critical micelle concentration and surface tension of anionic surfactant exclusively as well as in combination with xanthan gum or scleroglucan

	Surface tension		Interfacial tension	
	CMC (mol/L)	γ_{cmc} (mN/m)	CMC (mol/L)	γ_{cmc} (mN/m)
Anionic surfactant	$5.03 \cdot 10^{-04}$	36	$2.87 \cdot 10^{-04}$	7
Xanthan gum and anionic surfactant	$8.61 \cdot 10^{-04}$	34	$7.90 \cdot 10^{-04}$	5
Scleroglucan and anionic surfactant	$7.18 \cdot 10^{-04}$	32	$8.61 \cdot 10^{-04}$	3

anionic surfactants screen electrostatic repulsive interactions along the polyelectrolyte backbone, resulting in polymer retraction and reduced inter-chain entanglement. Non-electrostatic interactions are also evident between xanthan gum and surfactants. Based on diminishing viscosity reduction activity at moderate and high shear rates, it is evident that non-electrostatic polymer-surfactant interactions act primarily on the inherent backbone structure of xanthan gum, instead of affecting side-chain association behavior. Non-electrostatic interactions likely promote a structural transition from a rigid ordered double helix to a weaker and less ordered conformation. Binding of the anionic surfactant to the xanthan gum backbone is confirmed by interfacial tension measurements.

In contrast to xanthan gum, the helical structure of scleroglucan does not undergo transitions below 135°C. Surfactant interactions with scleroglucan result in a viscosity increase, a portion of which span the entire shear rate regime. The viscosity increases occur also under electrostatically screened conditions, suggesting non-electrostatic effects such as hydrodynamic volume effects and imparted inter-molecular association effects. Interfacial tension measurements confirm anionic surfactant binding to scleroglucan.

In conclusion, xanthan gum and scleroglucan are viable candidates for EOR polymer flooding, demonstrating the favorable viscosifying performance as well as shear and electrolyte tolerance. However, interactions with surfactants are non-trivial, and are dependent on the charge characteristics of the biopolymer.

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