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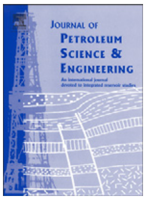

Dilute iota- and kappa-Carrageenan solutions with high viscosities in high salinity brines

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ABSTRACT

We evaluated the rheological characteristics of ι- and κ-Carrageenan in aqueous solutions. Viscosities strongly increased with increasing polymer concentration or salinity. Monovalent Na^+ cations were more effective in increasing viscosity than divalent Ca^{2+} cations. A more complex brine containing Na^+, Mg^{2+} and Ca^{2+} cations also showed high viscosities at a high salinity. We observed shear thinning behavior for these polysaccharide solutions. We explain these rheological phenomena with molecular processes, specifically the conformation change of the ι-Carrageenan from random coil to double helix.

In the context of enhanced oil recovery, ι-Carrageenan solutions can reach much higher viscosities at high salinities than standard polyacrylamide solutions. Moreover, Carrageenans are renewable, nontoxic, green substances.

1. Introduction

To address the increasing energy needs of society in the face of dwindling petroleum reserves it is essential to improve the materials used for enhanced oil recovery (EOR). In order to increase sweep efficiency during tertiary oil recovery, dilute aqueous polymer solutions are commonly used as mobility control agents (Ryles, 1983; Green and Willhite, 1998; Nasr-El-Din et al., 1991; Seright et al., 2009). These agents alter the mobility ratio of injected fluids to crude oil favorably, i.e. reduce viscous fingering by increasing the viscosity of the injected fluid. Moreover, by injecting a viscous fluid, the capillary number is increased which directly leads to improved oil recovery (Abrams, 1975; Green and Willhite, 1998).

The industrial standard for such applications are dilute polyacrylamide (PAM) or Xanthan gum aqueous solutions, which have been in widespread use for several decades (Green and Willhite, 1998). Moreover, at higher concentrations (above 4000 ppm), PAM can form a viscous gel if formulated with Cr^{3+} or analogous cross-linking agents (Dona et al., 1996; Jain et al., 2005). PAM gels have very high viscosities reaching 800–8000 Pa s (Sydansk, 1992); which has made them useful as a near-wellbore fluid (Sydansk, 1992; Green and Willhite, 1998), a fracturing fluid (Weinstein et al., 2009) or as a tool for in-depth blockage of high permeability regions of rocks in heterogeneous reservoirs (Smith, 1995).

Unfortunately, these PAM and Xanthan solutions have serious limitations. Thus they have fairly low resistance against elevated temperatures (polymer degradation) (Ryles, 1983; Yang, 1998) and a viscosity that decreases strongly with increasing salinity for PAM (Martin and Sherwood, 1975; Green and Willhite, 1998) and remains almost constant in case of Xanthan (Green and Willhite, 1998). In addition for calcium concentrations above a few hundred ppm (200 ppm) for a 1000 ppm PAM solution (Levitt and Pope, 2008), PAM is subject to precipitation by calcium. Thus Scott (1983) states that shear stability and salinity tolerance to multivalent cations significantly reduces application possibilities of PAM solutions.

We will show that calcium is actually beneficial in reaching high viscosities in the presented case.

In this work we address this salinity limitation especially of PAM and present a class of polymers where viscosity increases with increasing salinity. This is the Carrageenan class of polymers, a renewable, ecological and nontoxic green substrate. Carrageenans are currently used industrially in the food, cosmetics, toothpaste, pharmaceutical, and beverages industries (Stoloff, 1959; Glicksman, 1962; Zabik and Aldrich, 1967; CP Kelco, 2004; Reeve et al., 2006) in large quantities.

Carrageenans are polysaccharides extracted from red seaweed species of the class Rhodophyceae (Stoloff, 1959; Rees, 1969; Rochas

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et al., 1989). They are built from α-1,3 and β-1,4 linked galactan units to form linear anionic sulfated polysaccharides. They are classified according to the presence of the 3,6-anhydrogalactose on the 4-linked residue and the position and number of the sulfate groups (Rees, 1969; Rochas et al., 1989). Carrageenans have been studied extensively (Zabik and Aldrich, 1965, 1967; Bellion et al., 1981; Phillips et al., 1986; Watase and Nishinari, 1986; Ridout et al., 1996; Ross-Murphy, 1991), especially in the context of the food industry, but not in the context of EOR.

Several different Carrageenan types have been identified including ι-, κ-, λ- or μ-Carrageenans, but we focus here on κ- and ι-Carrageenan, which form thermally reversible polymer gels at low aqueous solution concentrations (1 wt.%) (Stoloff, 1959; Rees, 1969; Clark and Ross-Murphy, 1987; Rochas et al., 1989). We do not investigate the non-gelling (but thickening) λ-Carrageenan, which has been studied extensively in the literature. The gelling mechanism for κ- and ι- Carrageenans stems from the self-association of the polymer molecules into three-dimensional networks cross-linked by isolated double helices (Rees, 1969; Picullel et al., 1997), a mechanism we discuss in more detail below. Carrageenans undergo hydrolysis at $pH<3.5$ (Stoloff, 1959), so we consider higher pH conditions. In addition, we investigated the heat stability of Carrageenan (Masson, 1955; Masson et al., 1955), where we find a first-order random heat degradation of the polymer with a reaction velocity constant $k=2.75\times10^{13}\exp(-29{,}200/RT)\ h^{-1}$.

We show here that ι- and κ-Carrageenans are attractive green substitutes for PAM for EOR applications under high salinity conditions. Our main focus here is on ι-Carrageenan because the presence of two sulfuric ester groups leads to lower gel formation concentrations and higher viscosities than κ-Carrageenans (Chronakis et al., 1996; Picullel et al., 1997). This notion is consistent with measurements by Duran et al. (1986), who observed that ι-Carrageenan gels have higher maximum rupture strengths and higher apparent Young's moduli than comparable κ-Carrageenan gels. The target of our work was to determine formulations involving low polymer concentrations that would reduce costs for EOR applications.

We tested the influence of polymer concentration, shear rate, salinity and ionic strength on the fluid's viscosity. Even a small shear rate dependency can have significant implications for petroleum engineering applications since it influences injection pressures and near-wellbore flow (Green and Willhite, 1998). We also consider the dependence of the viscosity on cation types and concentrations and on temperatures since brines in geological formations can be expected to vary significantly.

2. Experimental methods

2.1. Materials

We purchased κ-Carrageenan (CAS number: 9064-57-7, type I) and ι-Carrageenan (CAS number: 9062-07-1, type II) from Aldrich, the chemical structures are presented in Fig. 1.

ι-Carrageenan and κ-Carrageenan are linear polysaccharides constructed of repeated 1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-D-galactopyranose units. ι-Carrageenan contains two sulfate groups [→3)-α-D-galactose-6-sulfate-(1→4)-β-D-3,6-anhydrogalactose-2-sulfate-(1→] and κ-Carrageenan one sulfate group per disaccharide unit [the 2-sulfate substituent on the anhydrogalactose residue is absent] (Rees, 1969; Ridout et al., 1996).

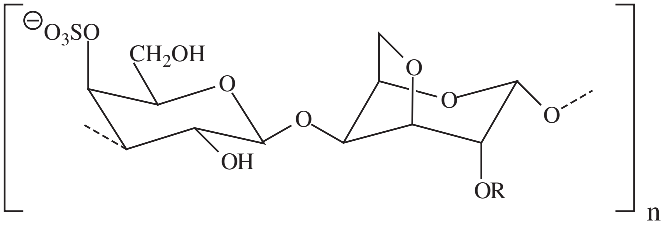

Fig. 1. Molecular structure of Carrageenan, $R=SO_3^-$ for ι-Carrageenan, $R=H$ for κ-Carrageenan (Anderson et al., 1968; Rees, 1969; Viebke et al., 1995).

Sodium chloride, potassium chloride, magnesium chloride and calcium chloride were purchased from Aldrich (ACS grade). The deionized water was prepared in-house by distilling tap water twice.

2.2. Experimental procedure

Carrageenan solutions were prepared by dissolving Carrageenan in deionized water at elevated temperature (70 °C) under agitation and then adding brine while continuing stirring for 30 min. Brine concentrations were calculated and the brine was prepared in such a way that the desired final concentrations were reached. The samples were then cooled to ambient conditions (i.e. 25 °C and atmospheric pressure) and the solutions were stirred for another 24 h. The mixing process was conducted in a closed system (sealed glass).

Three cations (Na^+, Mg^{2+} and Ca^{2+}) were used for preparing ι-Carrageenan solutions and K^+ was used for the preparation of the κ-Carrageenan solution. The cations were added in the form of the chloride salt to deionized water for brine preparation. Salinities of these salts were varied from 0 to 20 wt.%, covering most geologically relevant salinities.

Zabik and Aldrich (1965) reported no influence of anion type on the viscosity of λ-Carrageenan solutions. We held the anion type constant (chloride), and did not further investigate anion effects in this work.

The viscosities of the polymer solutions were then measured at different shear rates (0.5, 1 2, 5, 10, 20, 50, and 100 rpm, which is equivalent to shear rates of $0.65\ s^{-1}$, $1.3\ s^{-1}$, $2.6\ s^{-1}$, $6.5\ s^{-1}$, $13\ s^{-1}$, $26\ s^{-1}$, $65\ s^{-1}$, and $130\ s^{-1}$) with a Brookfield DV-E viscometer and a #18 spindle at atmospheric pressure and a temperature of 25 °C. For some experiments the temperature was varied as stated.

3. Results and discussion

As expected increasing polymer concentration leads to a strong increase in viscosity, consistent with earlier measurements for κ-Carrageenan (Stoloff, 1959; Picullel et al., 1997), many other polysaccharides (Clasen and Kulicke, 2001), and polymers in general (Elias, 1997). In the following we will discuss the influence of cation type and concentration, ionic strength, shear rate, temperature and ageing.

3.1. Influence of cation type and cation concentration on viscosity

The influence of $CaCl_2$ concentration on the viscosity of 5000 ppm ι-Carrageenan brine solution is displayed in Fig. 2. The viscosity increases strongly with $CaCl_2$ concentration, especially above 3 wt.%, reaching circa a tenfold increase at a $CaCl_2$ concentration of 20 wt.%.

The reason for this very strong, almost exponential, viscosity increase with salinity is that the ι-Carrageenan molecules aggregate when Ca^{2+} cations are added. The Ca^{2+} cations shield the electrostatic repulsion induced by the sulfate groups between the ι-Carrageenan molecules. This molecular mechanism is discussed below in more detail.

In contrast, PAM systems show a strong reduction of viscosity with an increase in salinity (Mungan, 1972; Nasr-El-Din et al., 1991; Green and Willhite, 1998; Levitt and Pope, 2008), while the viscosity of Xanthan solutions was almost constant as a function of salinity (Auerbach, 1985).

The rheological characteristics we have observed for ι-Carrageenan solutions at these conditions are highly useful for EOR applications, especially for reservoirs with high divalent cation content in which