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.

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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 polyacryl-amide (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 $k = 2.75 \times 10^{13} \exp(-29,200/RT)$ 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-
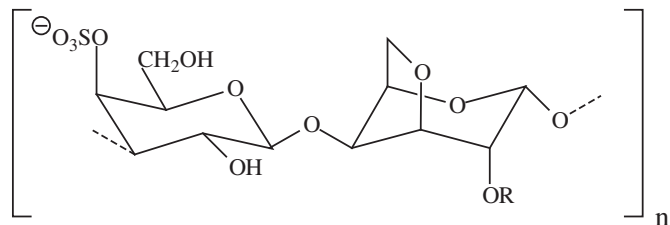
linked 3,6-anhydro-D-galactopyranose units. ι-Carrageenan contains two sulfate groups [→3)-α-D-galactose-6-sulfate-(1→4)-β-D-3,6-anhydrogalactose-2-sulfate-(1→] and κ-Carrageenan one sulfate group per disaccharide unit [the 2-sulfate substituent on the anhydrogalactose residue is absent] (Rees, 1969; Ridout et al., 1996).

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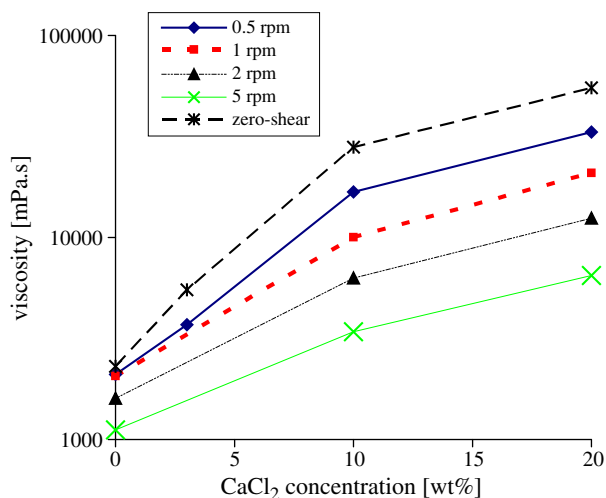
Fig. 1. Molecular structure of Carrageenan, $R = SO_3^-$ for ι-Carrageenan, $R = H$ for κ-Carrageenan (Anderson et al., 1968; Rees, 1969; Viebke et al., 1995).

Fig. 2. Influence of CaCl₂ concentration and shear rate on the viscosity of 5000 ppm ɩ-Carrageenan brine solution.

PAM cannot be successfully applied. We find that at very high CaCl₂ concentrations (10–20 wt.% CaCl₂ solutions) the viscosity for ɩ-Carrageenan reaches 30–60 Pa s .

Fig. 3 presents the viscosity of 5000 ppm ɩ-Carrageenan solutions in CaCl₂/NaCl brine for different shear rates, while holding the total salinity constant at 3 wt.%. We see that increasing Na⁺ concentrations lead to a massive increase in viscosity.

This data indicates that ɩ-Carrageenan formulations are extremely efficient when Na⁺ concentrations are high. We hypothesize that this favorable rheological behavior can also be achieved with other monovalent cations, especially for those which have a similar charge-to-volume ratio. This hypothesis is based on the gelling mechanism described below and data reported for κ-Carrageenan. Moreover, we hypothesize that more concentrated Carrageenan solutions can reach very high viscosities comparable to PAM-Cr³⁺ gels, especially at high salinities. Such gels could be used instead of the PAM-Cr³⁺ gels in particular in high salinity regions.

Watase and Nishinari (1982) reported a strong increase of the storage modulus of κ-Carrageenan gel after immersion into an alkali metal salt solution. They attributed this increase to the shielding effect of the electrostatic repulsion of sulfate groups by alkali metal ions. Again, this gelling mechanism is discussed in more detail below. Watase and Nishinari (1986) concluded that alkaline earth- and alkali metal cations act in an analogous way in terms of initiating the gelling of κ-Carrageenan solutions.

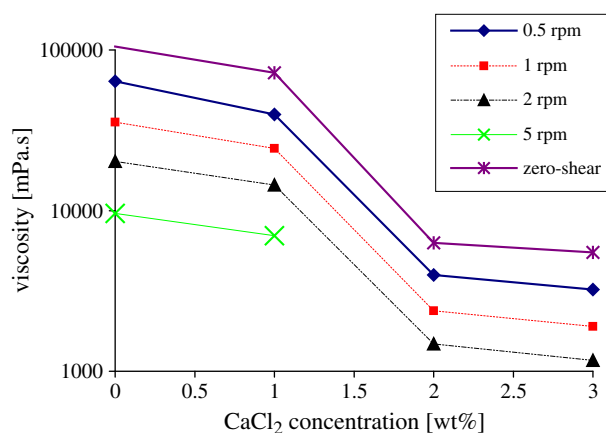Zabik and Aldrich (1967) found that the viscosity of λ-Carrageenan decreased with increasing salinity. This is opposite to our findings for ɩ-Carrageenan. The difference in Zabik and Aldrich's results and ours apparently lies in the difference of the polysaccharide structure (λ-Carrageenan with only galactose units does not form gels, Rochas et al., 1989) and/or in the preparation method. During Zabik and Aldrich's preparation of the Carrageenan this polymer might have been degraded and/or changed.

In comparable PAM systems, Nasr-El-Din et al. (1991) and Levitt and Pope (2008) recorded a strong viscosity reduction when CaCl₂ was present (as compared to only NaCl brine). Precipitation of PAM-calcium complexes were identified by Levitt and Pope (2008) and Moradi-Araghi and Doe (1987). Such precipitation not only leads to a viscosity reduction of the polymer solution, but also to serious problems regarding the blockage/permeability of the pore-network structure.

3.2. Influence of anion type on viscosity

Zabik and Aldrich (1965) showed that the anion type has no influence on the viscosity of λ-Carrageenan solutions. Based on this observation and taking into account the molecular gelling mechanism (described below), we conclude that the anion type will have no or only a very minor effect on viscosities of aqueous κ- or ɩ-Carrageenan solutions. We therefore did not attempt to study this parameter further.

3.3. Viscosities of ɩ-Carrageenan solutions in synthetic reservoir brine

Viscosities of ɩ-Carrageenan solutions in a synthetic reservoir brine were analysed as this is industrially most relevant for EOR applications. Reservoir brines are complex mixtures of various dissolved salts of varying concentration, and specific compositions depend on the exact geographical location. To approximate the brine composition found in the Shengli oil field in China (cp. Table 1) we prepared a brine which contained 30,000 ppm NaCl, 1320 ppm CaCl₂·2 H₂O and 2140 ppm MgCl₂·6 H₂O. The density of this brine was measured to be 1015 kg/m³. We kept the anion type constant (chloride) to exclude eventual effects of anion type on viscosity and/or gelling.

Fig. 4 presents how the viscosity of ɩ-Carrageenan solutions in synthetic Shengli brine responded to changes in polymer concentration and/or shear rate. Measurement conditions were 85 °C at atmospheric pressure. Consistent with our previous results the viscosity strongly increased with polymer concentration. Polymer concentrations ranging from 2500 ppm to 4000 ppm generated comparatively high viscosities (60–320 mPa s) at low shear rates, while the viscosity of a 5000 ppm ɩ-Carrageenan solution jumped up to circa 4000 mPa s which is very high if compared to PAM or Xanthan at these physico-chemial conditions. Application of such a fluid for mobility control or at a higher polymer concentration for near-wellbore treatment might be feasible, especially in high salinity brines with high divalent cation concentration.

In summary, the ɩ-Carrageenan solutions all showed high viscosities in the synthetic Shengli brine which contained three

Fig. 3. Influence of NaCl/CaCl₂ concentration ratio and shear rate on the viscosity of 5000 ppm ɩ-Carrageenan brine solution (salinity was constant at 3 wt.% salt).

Table 1
Water analysis of Chengdao oilfield brine composition, I = ionic strength.

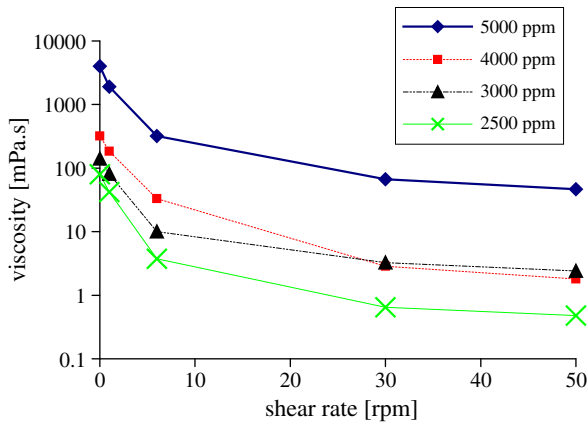| Anion	Conc. [mg L⁻¹]	Cation	Conc. [mg L⁻¹]
HCO₃⁻	85.88	Mg²⁺	1115.43
Cl⁻	16,284.84	Ca²⁺	357.61
SO₄²⁻	2229.68	Na⁺ + K⁺	9144.041
SUM	18,600.4	SUM	10,617.081
TDS [mg L⁻¹]			29,217.481
I [mol/L]			0.5484
pH			7
density [kg m⁻³]			1014

Fig. 4. Shear rate dependence and influence of polymer concentration on viscosity of ι-Carrageenan in synthetic Shengli brine at 85 °C.

different cations and chloride anions at a realistic high reservoir salinity (TDS was approximately 30 g salt/L, cp. Table 1). We hypothesize that the ι-Carrageenan solutions will also show high viscosities if additional cations and/or anion types are introduced. This is again based on the gelling mechanism described below.

Our data is consistent with Stoloff's analysis (1959), where an increase in mechanical gel strength of κ-Carrageenan with increase in K$^+$ or Ca^{2+} concentration was recorded.

Contrary to the rheological behavior of ι-Carrageenan, Levitt and Pope (2008) observed a strong decrease in 1500 ppm PAM solution viscosity with increase in NaCl salinity. This viscosity decrease was particularly drastic when shifting the salinity from 0 ppm NaCl to circa 10,000 ppm NaCl. Nominally, viscosities were reduced from 40 to 75 mPa s (they investigated different PAM products) to 10–30 mPa s. Of course salinities of oil reservoirs are higher which reduces the EOR efficiency of PAM. Even worse (viscosity-reducing) effects were observed for NaCl/CaCl$_2$ brines.

Xanthan solution viscosity is unaffected by changes in salinity (Auerbach, 1985); Xanthan solutions in CaCl$_2$ or NaCl brine had fairly constant viscosities (at a polymer concentration of 500 ppm 10–15 mPa s and at 750 ppm 18–26 mPa s, measured at 6 rpm over a salinity range 0–10 wt.%, Green and Willhite, 1998).

3.4. Influence of ionic strength of brine on viscosity

We replotted the same viscosity data presented in the previous section as a function of ionic strength I (cp. Fig. 5). Though an increase in ionic strength led to higher viscosities if the cation (=Ca^{2+}) (and

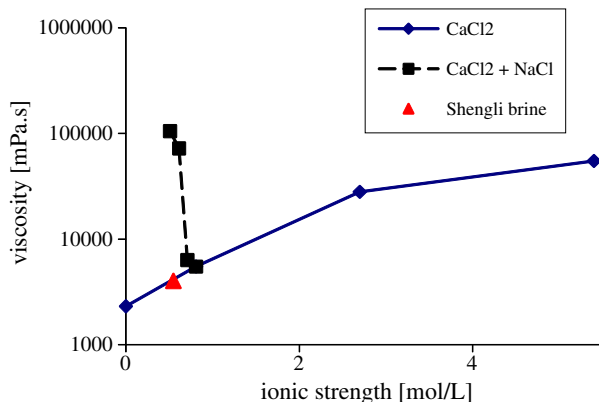anion) was constant, the viscosity decreased with ionic strength in case of a brine containing Na$^+$ and Ca^{2+} ions. This again highlights that the cation type has a major influence on viscosity, but also that ionic strength and with it a parameter quantifying concentrations of electrical charges in the solution are insufficient to easily predict the rheological behavior of these solutions. We hypothesize that Na$^+$ leads to a much stronger Carrageenan molecular aggregation and double helix formation generating higher viscosities than Ca^{2+}. The reason for this might be stronger quantum mechanical interactions Na$^+$–SO$_4^{2-}$ (as compared to Ca^{2+}–SO$_4^{2-}$) in the aqueous Carrageenan brine solution environment, but this needs further evidence in form of experimental molecular data and/or quantum mechanical calculations.

A loss of viscosity with an increase in ionic strength was cited as a major problem in terms of the application of PAM solutions as EOR agents by Auerbach (1985). Xanthan however keeps an almost constant viscosity versus ionic strength (Auerbach, 1985).

3.5. Influence of temperature on viscosity

Fig. 6 displays how the viscosity of a 4000 ppm ι-Carrageenan solution in synthetic Shengli brine exponentially decayed with increase in temperature. The shear rate was 6 rpm throughout. The trendline plotted through the experimental datapoints is a least-square fit, the function is printed into the plot. This observation is consistent with literature data (Stoloff, 1959) and data presented by Picullel et al. (1997) for κ-Carrageenan gels; Picullel et al. (1997) recorded a strongly decreasing storage- and loss modulus with increasing temperature.

The viscosity is still relatively high at 85 °C (ca. 50 mPa s), which is the target temperature for the Shengli oil field. Zero-shear viscosities will be substantially higher as indicated in Figs. 2–4. We conclude that ι-Carrageenan brine solutions can be applied in reservoirs with high salinity and maybe at elevated temperature. Further testing is required to evaluate the long-term chemical stability of ι-Carrageenan solutions at elevated temperatures.

This temperature-dependency is consistent with observations published by Chronakis et al. (1996) who measured a decrease in storage modulus, loss modulus and phase shift tan δ of sodium κ-Carrageenan solutions with increasing temperature. These rheological parameters also varied with type and concentration of alkali cations. Watase and Nishinari's observation (1986) that the dynamic Young's modulus decreased with increasing temperature for alkali earth metal κ-Carrageenan solutions also confirms this viscosity-temperature relationship. Watase and Nishinari (1986) found a maximum in the dynamic Young's modulus against earth alkali metal concentration for a 2 wt.% κ-Carrageenan solution.

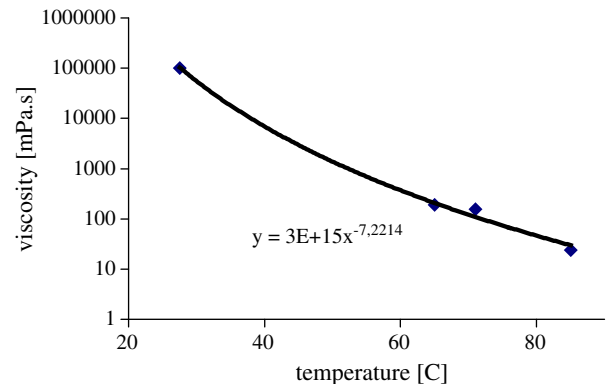**Fig. 5.** Viscosity of 5000 ppm ι-Carrageenan as a function of ionic strength of the brine.

$$y = 3E+15x^{-7,2214}$$

Fig. 6. Temperature dependence of viscosity of 4000 ppm ι-Carrageenan in synthetic Shengli brine (shear rate = 6 rpm).

An exponential decrease in viscosity with an increase in temperature is also found for cellulose derivatives (Clasen and Kulicke, 2001).

3.6. Gelling mechanism of ι- and κ-Carrageenan in aqueous salt solutions

Rees (1969), Rees et al. (1982) and Morris et al. (1980) described the gelling mechanism of ι-Carrageenan and κ-Carrageenan in brines. During gelation, the dissolved polymer random coils undergo a transition into a double helical conformation as depicted in Fig. 7. Depending on the cross-link density stronger gels can be formed (right side of Fig. 7). This mechanism was confirmed by gel permeation chromatography/multi-angle laser light scattering experiments (Viebke et al., 1995; Picullel et al., 1997), electron micrographs (Stokke et al., 1993) and cryo-transmission electron microscopy (Borgström et al., 1996). Rochas et al. (1989) analysed the molecular structures of ι- and κ-Carrageenan with infrared-, ^{1}H NMR-, ^{13}C NMR-spectroscopy and size exclusion chromatography and found that the domains in which ι-Carrageenan and κ-Carrageenan are in the random coil or the helical conformation are different and consequently the gelling ability of the two polymers is different; these conformational domains can be controlled by temperature and/or electrolyte concentration (Rochas et al., 1989; Viebke et al., 1995). It is claimed that the formation of κ-Carrageenan gels is reversible (Viebke et al., 1995).

The gelling mechanism is extremely sensitive to the fine structure of the polysaccharide (Rees, 1969) and tight helix–helix aggregation only occurs in the presence of cations which shield the electrostatic repulsion between the sulfate side groups (Watase and Nishinari, 1982). This gelling mechanism is also reflected in rheological properties, where changes in storage modulus and intrinsic viscosity were observed (Watase and Nishinari, 1982).

3.7. Influence of shear rate on viscosity

All investigated ι-Carrageenan solutions showed a strong shear thinning behavior. We explain this with the mechanical destruction of the aggregates, basically the cross-linked junctions (cation-sulfate group) are torn apart by mechanical force.

Our results are consistent with shear thinning behavior observed for κ-Carrageenan solutions (Stoloff, 1959). Masson and Caines (1954) and Masson and Goring (1955) recorded non-Newtonian flow behavior for high molecular weight Carrageenan solutions.

Moreover, such shear-thinning behavior is generally observed for aqueous cellulose systems (Clasen and Kulicke, 2001) and biopolymer systems (Hughes et al., 1990).
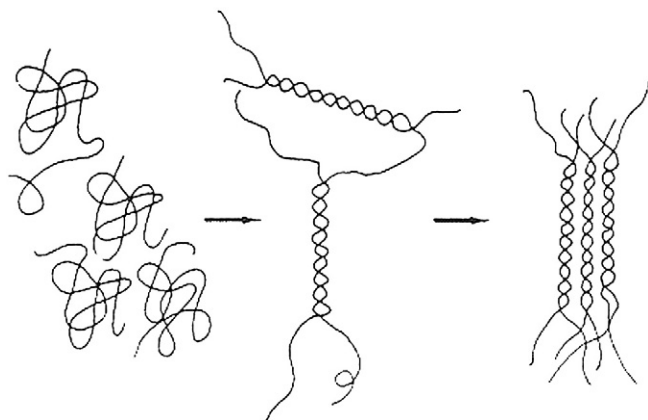
Strong shear-thinning behavior is also a well-known characteristic of PAM solutions (Green and Willhite, 1998, Nasr-El-Din et al., 1991, Mungan, 1972). As an example, Nasr-El-Din et al. (1991) measured a viscosity reduction from 9000 mPa s to 200 mPa s for a 1000 ppm PAM solution at 20 °C in 0.01 wt.% NaCl brine when the shear rate was increased from $0.02\ s^{-1}$ to $1\ s^{-1}$. This effect was marginalized however when the brine salinity was increased to 8.2 wt.% NaCl — at such a salt concentration, the viscosity of the same system was much lower (10 mPa s) and almost independent of the shear rate (range 0.05–$1\ s^{-1}$); a small reduction in viscosity down to 7 mPa s was observed when increasing the applied shear rate further to $100\ s^{-1}$.

Scott (1983) claims that one advantage of biopolymers over PAM solutions is that they show a good shear stability.

3.8. Viscosities of highly dilute ι- and κ-Carrageenan aqueous solutions

The viscosity of very dilute ι-Carrageenan (500 ppm in 10 wt.% NaCl/1 wt.% CaCl$_2$ brine) and κ-Carrageenan (250 ppm in 10 wt.% KCl brine) solutions is presented in Fig. 8 as a function of shear rate. Measurements were conducted at a temperature of 25 °C and atmospheric pressure. Least square fits are added; Eq. (1) shows the fit for the ι-Carrageenan solution, and Eq. (2) the fit for the κ-Carrageenan solution; the viscosity exponentially decreased with increasing shear rate. Polymer solutions at these low concentrations are highly relevant as mobility control agents in the oil industry.

$$y = 6.5598x^{-0.3031} \tag{1}$$

$$y = 11.605x^{-0.4782} \tag{2}$$

We measured a viscosity of 1.5 mPa s for a 350 ppm PAM (Alcoflood 1235) solution in 2 wt.% NaCl brine at the same thermodynamic conditions (measured at 2 rpm). If compared to this measurement, both Carrageenans had a viscosity which was higher by circa a factor of 4–7 even at a much higher salinity. This is very interesting as this means that an aqueous κ- or ι-Carrageenan solution is the better performing EOR fluid under these conditions. In other words, lower Carrageenan concentrations can achieve the same viscosities as PAM and costs can be reduced. We also expect chemical stability of Carrageenans at this temperature.

Other researchers reported that PAM solutions (600 ppm polymer concentration, measured at 6 rpm and 25 °C in 2 wt.% NaCl brine) reached viscosities in the range 3–5 mPa s, slightly depending on the degree of hydrolysis of the PAM (Green and Willhite, 1998).

Xanthan solutions showed viscosities similar to the Carrageenan solutions, e.g. 8–15 mPa s for a 500 ppm Xanthan solution measured
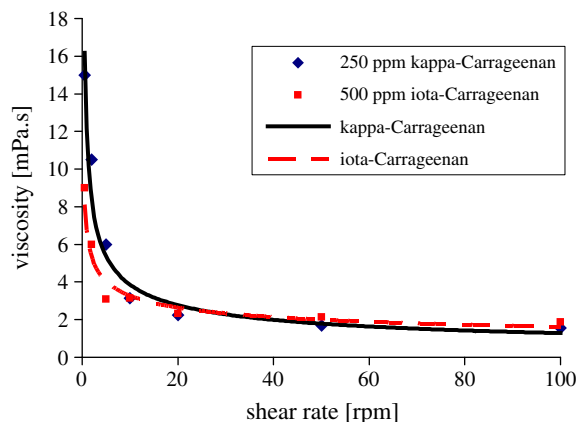

Fig. 7. Gelling mechanism of ι-Carrageenan and κ-Carrageenan gels (Rees, 1969).

Fig. 8. Viscosity of highly dilute κ-Carrageenan and ι-Carrageenan aqueous solutions as a function of shear rate.

at 6 rpm over a range of 1–100,000 ppm NaCl or CaCl₂ (Green and Willhite, 1998). Auerbach (1985) and Scott (1983) recorded viscosities of highly dilute Xanthan solutions in a similar range (circa 10–40 mPa s within a salinity range 0–20 wt.% salt and slightly higher polymer concentrations of 500–1000 ppm). Leveratto et al. (1995) also observed similar viscosities for similar biopolymer systems (3–30 mPa s for 200–1000 ppm polymer concentrations).

Viebke et al. (1995) found that at sufficient dilution, ι-Carrageenan has a monomolecular structure, i.e. the bimolecular helical conformation changes at very dilute polymer concentrations. This is consistent with our rheological observations where zero-shear viscosities of ι-Carrageenan were in the range of 10 mPa s, similar to Xanthan, which does not undergo the gelling mechanism displayed in Fig. 7.

3.9. Effect of ageing on solution viscosity

Viscosities of aqueous 5000 ppm ι-Carrageenan solutions aged for different time periods at ambient conditions are plotted in Figs. 9 and 10 as a function of shear rate and salt concentration. While in the 10 wt.% CaCl₂ solution in Fig. 9 no noticeable ageing effect was detected, viscosities of 5 wt.% CaCl₂ solutions were reduced after ageing.

No ageing effect was observed in 20 wt.% CaCl₂ brine solutions and a small increase in viscosity was recorded for 10 wt.% CaCl₂ brine solutions in Fig. 10. Deionized water and 3 wt.% CaCl₂ brine polymer solution datapoints are added to the graph as a baseline.

In summary, ageing effects were very small except for the 5 wt.% CaCl₂ brine solution. It might be that at this specific Ca²⁺ concentration the gel relaxes after initial formation.

Rochas et al. (1989) recorded an increase in yield stress for ι-/κ-Carrageenan blends after ageing for one week as compared to ageing overnight. However, they did not observe a significant difference in the Young's modulus for these systems of different age. This is in principle consistent with our results though not directly comparable. Zabik and Aldrich (1965) found a minimal influence of ageing time on viscosities of λ-Carrageenan solutions.

For PAM solutions, Ryles (1983) observed a substantial viscosity increase at low to medium salinities after ageing; however these increases were nominally small, e.g. a 1000 ppm PAM solution increased its viscosity from 20 mPa s to 30 mPa s after 14 days of ageing in an anaerobic environment (measured at 90 °C and 6 rpm). Levitt and Pope (2008) however observed only marginal ageing effects for 1500–2000 ppm PAM solutions in 30,000 ppm NaCl brines (ageing time = 200 days). One reason for the difference in these results might be the addition of an oxygen scavenger (dithionite), which Levitt and Pope (2008) added to their PAM formulations.
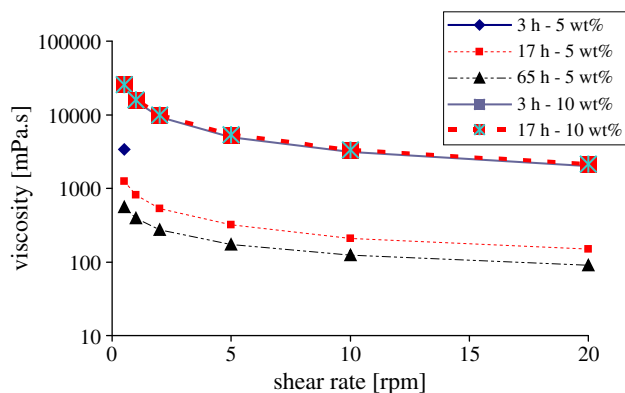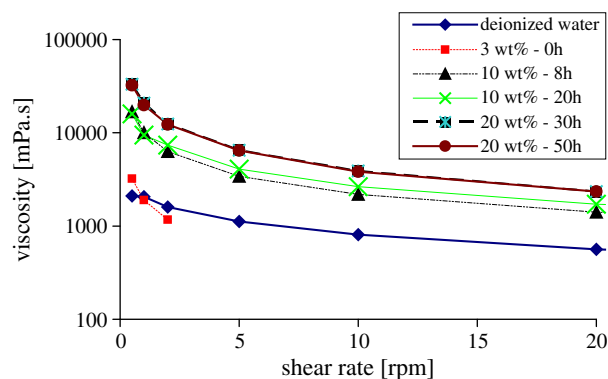

Fig. 10. Viscosity of 5000 ppm ι-Carrageenan in CaCl₂ brine or deionized water aged for different time periods.

Leveratto et al. (1995) recorded an ageing effect on viscosity for some biopolymers, but not for others.

3.10. Carrageenan solutions in deionized water

Above we established a strong dependence of ι-Carrageenan solution viscosity on cation concentration; the lower the salinity, the lower the viscosity. Thus we can expect that deionized water is a worst case scenario with respect to viscosity. Hence we proceeded next to study how viscosity changes when fresh water is injected. This is relevant for understanding how to clean up the gel in the subsurface while avoiding formation damage. Moreover, this adds to the understanding of the molecular mechanisms underlying the rheological behavior of these solutions while identifying minimum viscosities which are related to maximum injection pressures. The gelation mechanism described earlier for ι-Carrageenan cannot proceed without cations, which is the main reason for lower viscosities of deionized water-ι-Carrageenan solutions.

We measured viscosities of 100 ppm, 1000 ppm and 5000 ppm ι-Carrageenan solutions in deionized water as a function of shear rate (Fig. 11). As expected a small increase in polysaccharide concentration strongly increased the viscosity; all solutions showed shear thinning behavior.

The viscosity of 10,000 ppm ι-Carrageenan solution in deionized water exceeded the maximum number on the viscometer scale and was above 120,000 mPa s at 25 °C for all applied shear rates (0.5–100 rpm). For this solution also a strongly reduced viscosity was observed with an increase in temperature from above 120,000 mPa s to around 60 mPa s at 50 °C.

Masson and Caines (1954) and Katchalsky (1964) observed that Carrageenan molecules in dilute aqueous solutions of low ionic strength are rigidly extended whereas in the presence of electrolytes
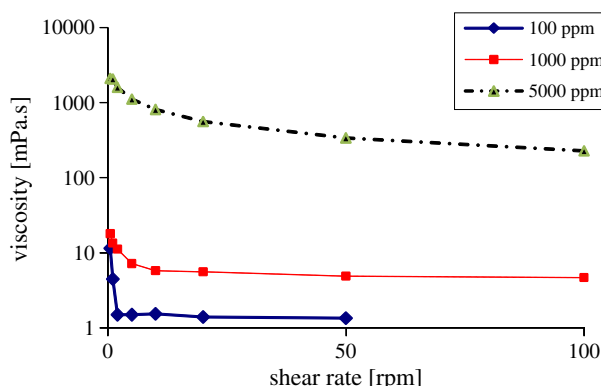

Fig. 9. Viscosity of 5000 ppm ι-Carrageenan in CaCl₂ brine aged for different time periods.

Fig. 11. Viscosity of ι-Carrageenan in deionized water.

the molecules are in a randomly coiled conformation. This is an additional factor which contributes to the massively reduced viscosity at low salt concentrations.

Viscosities of PAM solutions are significantly higher in deionized water than in brines (Nasr-El-Din et al., 1991, Mungan, 1972), roughly by an estimated factor of 100 based on results reported by these authors.

3.11. Influence of Carrageenan type on viscosity

Many different Carrageenan molecules have been identified, including ι-, κ-, λ-, μ-Carrageenan (Rees, 1969), however, only λ-, κ- and ι-Carrageenan are industrially relevant. λ- and κ-Carrageenan and to some extent ι-Carrageenan have been extensively investigated. As mentioned earlier, of these three main Carrageenans, only the ι- and κ-forms can generate gels. ι-Carrageenan solutions have higher viscosities than κ-Carrageenan solutions (Picullel et al., 1997; Chronakis et al., 1996).

At very dilute concentrations we found an almost identical rheological behavior of ι-Carrageenan and κ-Carrageenan solutions which can be explained by the dissociation of the gel into the monomolecular random coil structure and the similarity of the ι-Carrageenan and κ-Carrageenan molecules. Similar viscosities were also reported for dilute Xanthan solutions (Green and Willhite, 1998).

4. Conclusions

We studied the viscosities of aqueous ι-Carrageenan solutions with the objective of identifying formulations suitable for EOR applications; such an application for Carrageenan has not been previously discussed in the literature. We show that the viscosities of ι-Carrageenan solutions increase with an increase in salinity and that they can reach very high nominal viscosity values (to above 120 Pa s at 10,000 ppm polymer concentration), even at high brine salinities. Consequently, we conclude that ι-Carrageenan solutions would be useful as mobility control agents in reservoirs with high salinity, independent of salt type. Moreover, if sufficient cation moles are added such ι-Carrageenan solutions could replace PAM-Cr^{3+} gels for near-wellbore applications or as fracturing fluid. Carrageenans are renewable, nontoxic and not hazardous to the environment, making them "green" replacements for the current viscosity modifiers.

As polysaccharides are stable at high temperatures only for weeks (e.g. Xanthan for 2–3 weeks, Ryles, 1983), it is recommended that Carrageenan formulations be used only in high salinity reservoirs that exhibit low or moderate temperatures.

Key findings from this study include:

1. The viscosity of aqueous ι-Carrageenan solutions increases strongly with increasing salinity.
2. The viscosity of aqueous ι-Carrageenan solutions increases more strongly from addition of Na^+ cations than for Ca^{2+} cations.
3. Highly dilute κ-Carrageenan and ι-Carrageenan solutions (250–500 ppm) in high salinity brines have ~4 to 7-fold higher viscosities than a comparable PAM solution.
4. High viscosities were achieved with ι-Carrageenan solutions in a synthetic reservoir brine at elevated temperature.
5. An increase of temperature and shear rate strongly reduces the viscosities of ι-Carrageenan solutions.
6. Ageing effects on viscosity of ι-Carrageenan solutions are minimal.

Nomenclature

EOR   enhanced oil recovery
NaCl   sodium chloride
KCl   potassium chloride
$CaCl_2$ calcium chloride
$MgCl_2$ magnesium chloride
Mg^{2+} divalent magnesium cation
Ca^{2+} divalent calcium cation
Na^+ monovalent sodium cation
K^+ monovalent potassium cation
wt.%   weight %
rpm   revolutions per minute
ppm   parts per million
PAM   polyacrylamide
HCO_3^- hydrogencarbonate
Cl^- chloride
SO_4^{2-} sulfate
Cr^{3+} trivalent chromium cation
T   temperature
R   general gas constant [8.314 J K^{-1} mol^{-1}]
k   reaction velocity constant
TDS   total dissolved salt [mg L^{-1}]
I   ionic strength [mol/L]

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