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Influence of osmotic and weight pressure on water release from polysaccharide ionic gels

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ABSTRACT

Kappa-carrageenan (kC) is a polyelectrolyte biopolymer that forms gels if the kC concentration, the salt and the temperature are adequately chosen. Actually, under certain conditions, kC gels release water in a process called syneresis. In this contribution, the syneresis of gels containing 2 g/L of kC has been studied as a function of potassium chloride concentration [KCl]. The syneresis decreases if the [KCl] is increased in the biopolymer solution (sol) before the gelation but increases if the [KCl] is increased after gelation by immersing the gels in KCl solution. The surrounding phase induces an osmotic pressure (Π), which increases if the [KCl] difference between the inside and outside of the gel increases. Swelling has been observed for negative Π. A method that enables the exudate to be removed continuously demonstrated the effect of the strain caused by the gel's own weight on syneresis. Increasing the KCl concentration in the sol promotes syneresis due to strain. The analysis of the syneresis kinetics of different systems has enabled the creation of a pressure-induced syneresis diagram. This diagram will contribute to controlling the mouthfeel of chewing products.

1. Introduction

This work will demonstrate how the potassium chloride salt influences the release of water by syneresis in kappa-carrageenan (kC) gels, and, in particular, how the gel's own weight will also contribute to this water release. Kappa-carrageenan is a polyelectrolytic carbohydrate biopolymer (Borgström, Piculell, Viebke, & Talmon, 1996). This biopolymer is a sulfated polysaccharide that is extracted from seaweed and exhibits ion selectivity (Ciancia, Milas, & Rinaudo, 1997). This feature is demonstrated by the shift of some physical quantities, for example, the optical rotation (Mangione et al., 2005; Meunier, Nicolai, & Durand, 2000), gelation temperature and shear modulus, when different types of salts are used to study the behavior of this biopolymer in solution (Hermansson, Eriksson, & Jordansson, 1991; Lai, Wong, & Lii, 2000; Mangione et al., 2005). These physical quantities increased greatly if potassium is used instead of sodium. The effectiveness in increasing these physical quantities was found to follow a Hoffmeister series, i.e., $Rb^+ > Cs^+ > K^+ > Na^+ > Li^+$ (Ciancia, Milas, & Rinaudo, 1997; Morris & Chilvers, 1983). The syneresis of kC was found to also be influenced by this ion selectivity feature, particularly with regards to rheological testing (Hermansson et al., 1991; Lai et al., 2000; Richardson & Goycoolea, 1994). The gelation temperature and gel elasticity play important roles in the syneresis behavior; similarly, any factors that can change one of these two parameters will also, accordingly, affect syneresis. When kC gels become more elastic, they have a reduced degree of syneresis (Ako, 2015; Mao, Tang, & Swanson, 2001). A similar result is found for other gels. The higher the gel strength is, the smaller the syneresis effect becomes (Gerentes, Vachoud, Doury, & Domard, 2002). Although kC gels with sodium are elastically weak compared to those with potassium, their rheological measurement did not show a remarkable syneresis peak, as is seen for gels with potassium (Ako, 2015; Hermansson et al., 1991; Lai et al., 2000), which suggests that the elasticity alone does not explain the syneresis trend. The gel elasticity, as a result of ion selectivity, may govern the kinetics of the syneresis and, somehow, its extent.

Fluid secretion by internal organs and the contraction of smooth muscle in the presence of some types of salts are key components of a wide variety of biological processes (Drury & Mooney, 2003; Kershaw & Flier, 2004). The physiological mechanism that leads to secretion (Kershaw & Flier, 2004) and the physical mechanism that leads to syneresis are both complex (Mangione et al., 2007). However, their similarity offers a great perspective to understand the release phenomenon influenced by ion selectivity, given that the chemical compositions of polysaccharides are found in some extracellular matrices that surround internal organs and line various cavities in the body (Drury & Mooney, 2003).

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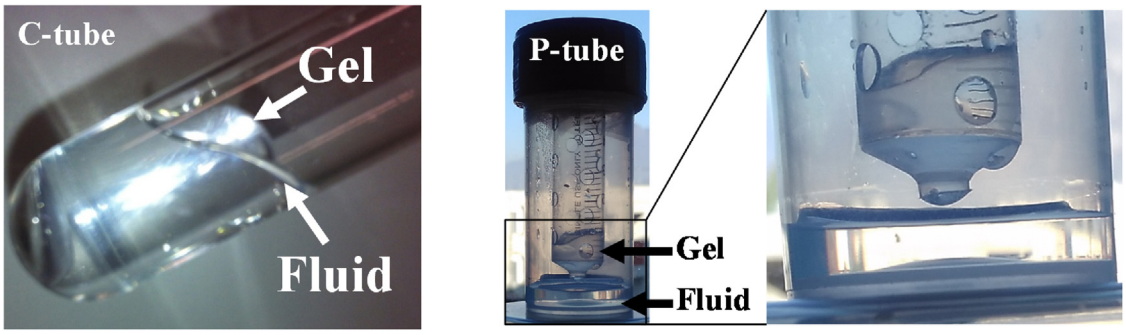

Fig. 1. A picture of gel showing the fluid released by syneresis in a closed tube (C-tube) and a perforated tube (P-tube).

This study will show how kC gels release fluid by syneresis under stress at different potassium concentrations. In this present work, two types of tubes were used to study the syneresis kinetics. One tube allows the released fluid to surround the gel and the other tube is perforated to readily remove the fluid from the surface of the gel. The total syneresis seems to consist of a term due to the shrinking mechanism and a term due to the strain caused by weight pressure. These two mechanisms are distinctly described by exponential decay functions because this function fits the experimental data well (Castillo, Lucey, Wang, & Payne, 2006). The exponential decay function that includes the terms accounting for shrinkage and stress has been used in the present work to interpret the experimental data.

2. Materials and methods

2.1. Gel preparation and syneresis measurement

The kC powder used in this work was kindly supplied by Cargill (France) in the pure potassium kC form. The powder, consisting of 3.9% (w/w) potassium, was used as received without further purification. A 10 g/L stock solution has been prepared by dissolving a small amount of the powder in hot water. The stock solution was filtered through 0.45-μm pore size Anotop filters before used.

The samples have been made by mixing an appropriate amount of the kC stock solution with 400 mM potassium chloride (KCl) stock solution. The mixture was homogenized during heating in a water bath at 90 °C for approximately 15 min, after which 5 ml of the mixture was poured into tubes (1.13 cm diameter and 6 cm height) and closed immediately to avoid evaporation. The closed tube (C-tube) was cooled in a refrigerator at (9 ± 2) °C to allow the gelation to occur. The gel formation was checked by inverting the C-tube to confirm that the meniscus did not flow; the time at which this was observed was defined as the gelation time. After several days, the fluid released from the gel, as shown on Fig. 1, was removed by syringe. All the samples contained 200 ppm sodium azide that was added as bacteriostatic agent.

After removing the fluid, the final weight of the gel (G_f) was measured with a balance with sensitivity = ±1 mg. The difference between the initial and final weight of the gel is divided by the gel's initial weight, and the value obtained is the syneresis, which is reported as a percentage, Eq. (1). Obviously, this value of the syneresis should not depend on the initial weight of the gel.

$$S_f = 1 - \frac{G_f}{G_i} \quad (1)$$

2.2. Syneresis kinetics measurement

The syneresis kinetics were measured at ≈ 9 °C using a perforated tube. This method consists of transferring the gel from the closed tube into the perforated tube, which has the same geometry. The P-tube is put in a transparent container and then sealed to avoid evaporation, as shown in Fig. 1 (P-tube). The container holds the P-tube raised to avoid contact with the exudate which collects at the bottom. The exudate in the container keeps the gel environment wet. The gel level in the P-tube was measured using the tube graduation with a precision of ± 0.1 ml, and the time was recorded, thus obtaining the syneresis kinetics. However, the syneresis at time zero cannot be accurately obtained with this experimental method, as this time point actually includes the true gelation time in the C-tube. Even if the accurate gelation time was known, the gels at this time cannot be treated. The time needed for the samples to gel in the C-tube with the inverting method was at least 30 min.

When the top side of the gel is retracting from the P-tube surface (see the zoom of the gel in P-tube of Fig. 1), the level of the gel is biased; thus, the weight of the gel was taken from this time. To avoid any mismatching between measuring the syneresis by weight and by volume, a calibration plot between the gel weight (W_{gel}) and volume (V_{gel}) was done, which gives the following equation: $W_{gel}\,(g) = 1.03\,V_{gel}\,(ml) + 0.05$.

2.3. Rheological measurements

The rheological measurements were performed using a DHR3 TA instruments Rheometers with an etched conic geometry (Ø 50 mm, 2.0°, TADC2°InR500) and an etched plate. A portion of the prepared hot-sample solution is loaded onto the Peltier plate of the rheometer and set at 65 °C, which is above the gelation temperature of the sample. After loading the sample, the surface is covered with a thin layer of mineral oil to avoid evaporation. The temperature was decreased to 10 °C at a rate of 2 °C/min and the strain and creep tests were conducted after the system had stabilised. At this temperature a true gel is formed, as shown by G' well above G". The strain measurements at 10 °C and 1 Hz were done to determine the strain at which the viscoelastic behavior of the gel changes. The creep test at 1 Hz was done by applying a constant stress and recording the time dependence of the strain.

3. Results and discussion

3.1. Effect of salt concentrations

A series of kC gels were kept at ≈ 9 °C for several days or weeks to determine the amount of water that was released. A previous measurement of the time evolution of the syneresis showed that one week is enough to stabilize the syneresis in C-tubes, and 15 days is enough for gels in P-tubes. However, if the gels are too soft, this time could be greater; therefore the series of kC gels at 2 g/L with different KCl concentrations were studied in duplicate, with one series being kept two weeks and the other being kept for almost one year. Fig. 2 shows the results of the syneresis from the gels at 2 g/L after