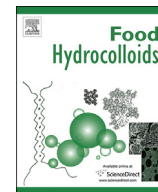




Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Effect of monovalent cations on calcium-induced assemblies of kappa carrageenan

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ARTICLE INFO

Article history:

Available online xxx

Keywords:

Kappa carrageenan
Differential scanning calorimetry
Calcium ions
Cation binding

ABSTRACT

The effect of Na⁺, K⁺ and Ca²⁺ cations on the thermal stability and aggregation of kappa carrageenan double helices has been explored by differential scanning calorimetry (DSC). Previous studies have shown that kappa carrageenan helices bind K⁺ cations, but not Na⁺. The kappa carrageenan used in this work was therefore in the Na⁺ salt form, to avoid complications from site-bound counterions to the polymer, and was studied at a fixed concentration of 1.0 wt % (~25 mN w.r.t. sulfate groups). Na⁺, K⁺ and Ca²⁺ cations were added as chloride salts. Values of peak-maximum temperature (T_{max}) in DSC cooling and heating scans (0.5 °C/min) increased progressively with increasing salt concentration, following the order Na⁺ < Ca²⁺ < K⁺, but greatest thermal hysteresis was seen with Ca²⁺. Our proposed interpretation is that Ca²⁺ cations "cement" the carrageenan helices together by binding directly between them, giving greater thermal stability, and thus greater hysteresis, than K⁺ cations which act indirectly by suppressing charge. On progressive addition of NaCl or KCl to solutions incorporating Ca²⁺ at concentrations of 5 mM or 12.5 mM (stoichiometric equivalence) the values of T_{max} moved asymptotically towards those seen for the same concentrations of the monovalent cations in the absence of calcium, suggesting progressive displacement of site-bound Ca²⁺. Thus T_{max} for the order–disorder transition was increased by KCl but reduced by NaCl, with the strange consequence that addition of NaCl lowered the transition temperature rather than raising it.

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1. Introduction

Kappa carrageenan is a structural polysaccharide from numerous species of red seaweed (Rhodophyta) and is used extensively as a gelling agent, particularly in food products (Glicksman, 1983; Stanley, 1990, pp. 79–119; Therkelsen, 1993, pp. 145–180).

It is one of a family of sulfated galactans (Painter, 1983, pp. 195–285) with primary structures based on a linear disaccharide repeating sequence of alternating 1,3 and 1,4-linked residues. The other gelling carrageenan used commercially is iota. In both iota and kappa carrageenan the 1,4-linked residues occur predominantly as the 3,6-anhydride (Fig. 1), and the 1,3-linked residues have a sulfate group at C(4). In nature, the anhydride bridge is absent in a significant proportion of the 1,4-linked residues, but in commercial production structural regularity is normally enhanced

by treatment with alkali (Smidsrød, Larsen, Pernas, & Haug, 1967; Stanley, 1963), giving structures close to the idealised repeating sequence in Fig. 1. Unlike kappa carrageenan, iota has an additional sulfate substituent at C (2) of the 1,4-linked residue (Anderson, Dolan, & Rees, 1973). Thus iota carrageenan has two negative charges per disaccharide, whereas kappa has only one.

This difference in pattern of sulfation causes profound differences in gelation behaviour. (Piculell, 1995, pp. 205–244). Iota carrageenan gels are formed on cooling by conversion of disordered coils to 3-fold double helices (Arnott, Scott, Rees, & McNab, 1974) which constitute the junction zones of the gel network (Rees, 1970). The coil–helix and accompanying sol–gel transitions are reversed on heating, with little, if any, thermal hysteresis.

Kappa carrageenan has a double helix structure similar to that of iota (Anderson, Campbell, Harding, Rees, & Samuel, 1969; Millane, Chandrasekaran, Arnott, & Dea, 1988). Again, gels form on cooling and melt on heating, but with substantial thermal hysteresis (in marked contrast to the sol–gel and gel–sol transitions of iota). Hysteresis is attributed to cation-induced aggregation of the kappa carrageenan double helices, with the aggregates surviving to higher

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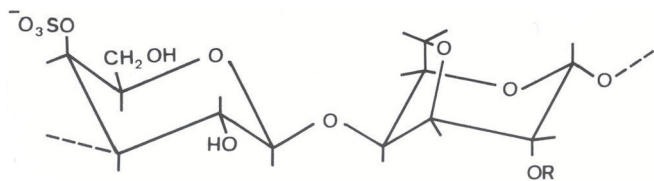


Fig. 1. Idealised disaccharide repeating structure of gelling carrageenans. R = H in kappa and SO_3^- in iota.

temperatures than those at which individual helices are formed on cooling (Morris & Norton, 1983, pp. 549–593; Morris, Rees, & Robinson, 1980). Some limited aggregation of helices, with associated slight thermal hysteresis, may also occur for iota carrageenan in the presence of high concentrations of Ca^{2+} cations (Goycoolea, Morris, & Gidley, 1995; Tari, Kara, & Pekcan, 2010).

It has been demonstrated by NMR (Belton, Morris, & Tanner, 1986; Grasdalen & Smidsrød, 1981; Piculell, Nilsson, & Ström, 1989) that, unlike Li^+ and Na^+ , K^+ (and larger Group I cations) bind to kappa carrageenan double helices. This reduces the net negative charge on the helices, and promotes helix–helix aggregation by suppressing electrostatic repulsion. Aggregation increases gel strength by giving an additional mechanism of crosslinking (Viebke, Piculell, & Nilsson, 1994), and commercial kappa carrageenan is therefore normally produced and supplied with K^+ as the predominant cation.

The interaction of kappa carrageenan with Ca^{2+} is less well understood. On addition of increasing concentrations of K^+ to 1.0 wt % solutions of kappa carrageenan in the Na^+ salt form (to avoid complications from site-binding of counterions to the polymer), Doyle, Giannouli, Philp, and Morris (2002) observed a large, monotonic increase in gel strength. With Ca^{2+} cations, by contrast, gel strength passed through a maximum at stoichiometric equivalence to the sulfate groups of the carrageenan. Maximum gel strength at stoichiometric equivalence of Ca^{2+} to the negative charge of the polymer has been observed subsequently (Doyle, Giannouli, Richardson, & Morris, 2018) for other concentrations of kappa carrageenan (in the range 0.5–3.0 wt %), suggesting that Ca^{2+} cations promote aggregation of the double helices by site-

binding between them (rather than by binding to individual helices, as happens with K^+).

In the present work, we have used differential scanning calorimetry to explore the effect of monovalent cations (K^+ and Na^+) on the stability of Ca^{2+} -induced aggregates of kappa carrageenan.

2. Materials and methods

Kappa carrageenan in the Na^+ salt form was kindly supplied by Quest International Ireland Ltd. Carrigaline, Co. Cork, Ireland. It is an alkali-modified extract from *Eucheima cottonii*, identical to the material used by Doyle et al. (2002) and Doyle et al. (2018). NaCl , KCl and CaCl_2 were AnalaR grade from BDH. Distilled deionised water was used throughout.

Differential scanning calorimetry (DSC) measurements were

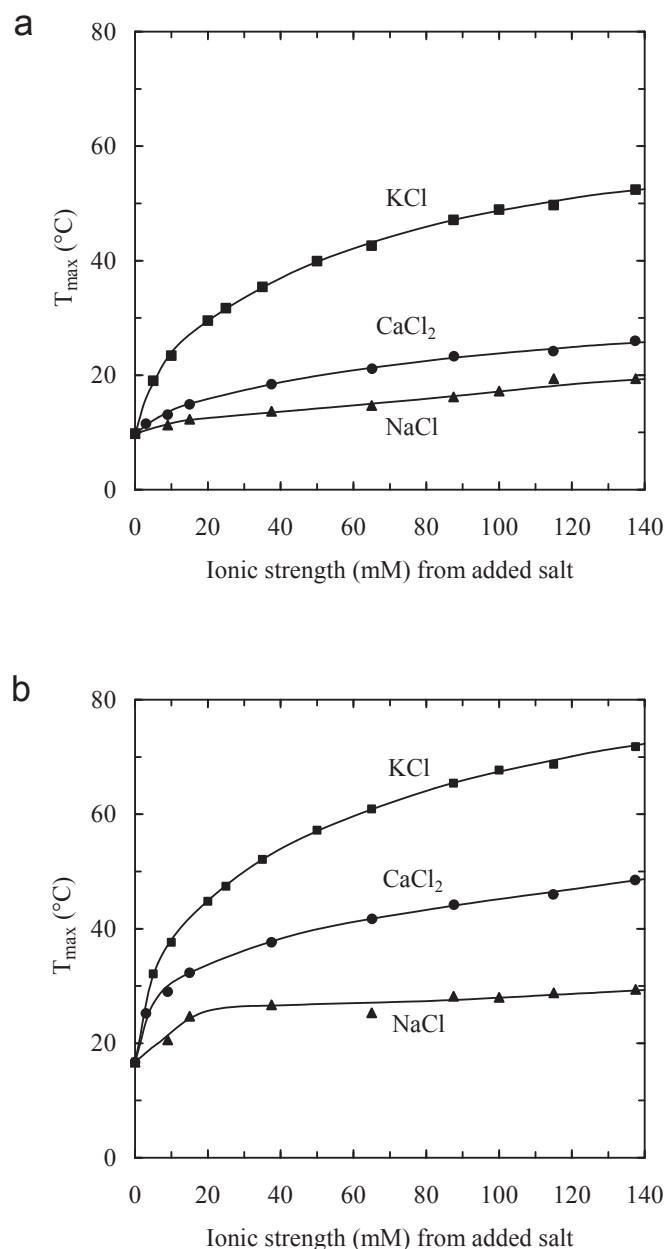


Fig. 3. Effect of ionic strength on peak-maximum temperature (T_{max}) for 1.0 wt % Na^+ kappa carrageenan on (a) cooling and (b) heating in the presence of increasing concentrations of NaCl (▲), KCl (■) or CaCl_2 (●).

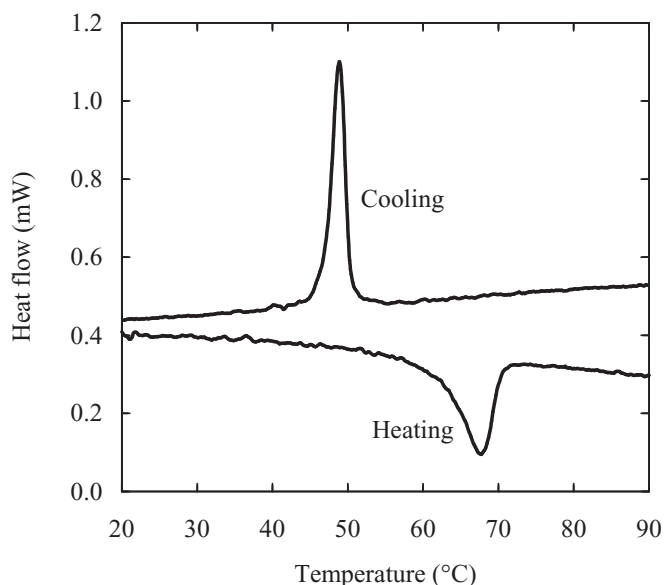


Fig. 2. DSC traces recorded on cooling and heating at $0.5^\circ\text{C}/\text{min}$ for 1.0 wt % Na^+ kappa carrageenan with 100 mM added KCl .

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