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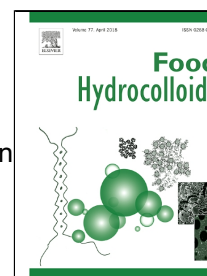
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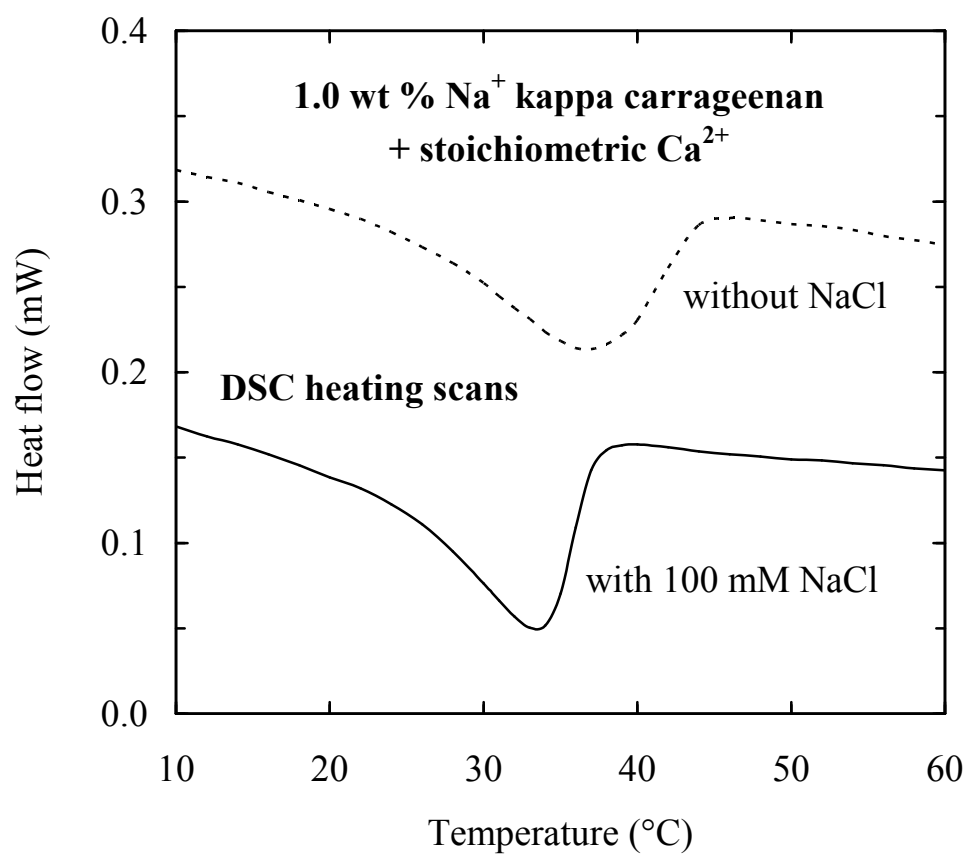


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Graphical abstract



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

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1 Abstract

2 The effect of Na^+ , K^+ and Ca^{2+} cations on the thermal stability and aggregation of kappa
3 carrageenan double helices has been explored by differential scanning calorimetry (DSC).
4 Previous studies have shown that kappa carrageenan helices bind K^+ cations, but not Na^+ .
5 The kappa carrageenan used in this work was therefore in the Na^+ salt form, to avoid
6 complications from site-bound counterions to the polymer, and was studied at a fixed
7 concentration of 1.0 wt % (~25 mN w.r.t. sulfate groups). Na^+ , K^+ and Ca^{2+} cations were
8 added as chloride salts. Values of peak-maximum temperature (T_{max}) in DSC cooling and
9 heating scans (0.5°C/min) increased progressively with increasing salt concentration,
10 following the order $\text{Na}^+ < \text{Ca}^{2+} < \text{K}^+$, but greatest thermal hysteresis was seen with Ca^{2+} .
11 Our proposed interpretation is that Ca^{2+} cations "cement" the carrageenan helices together by
12 binding directly between them, giving greater thermal stability, and thus greater hysteresis,
13 than K^+ cations which act indirectly by suppressing charge. On progressive addition of NaCl
14 or KCl to solutions incorporating Ca^{2+} at concentrations of 5 mM or 12.5 mM (stoichiometric
15 equivalence) the values of T_{max} moved asymptotically towards those seen for the same
16 concentrations of the monovalent cations in the absence of calcium, suggesting progressive
17 displacement of site-bound Ca^{2+} . Thus T_{max} for the order–disorder transition was increased by
18 KCl but reduced by NaCl, with the strange consequence that addition of NaCl *lowered* the
19 transition temperature rather than raising it.

20 Keywords

21 Kappa carrageenan; Differential scanning calorimetry; Calcium ions; Cation binding

23 1. Introduction

24 Kappa carrageenan is a structural polysaccharide from numerous species of red seaweed
25 (Rhodophyta) and is used extensively as a gelling agent, particularly in food products
26 (Glickman, 1983; Stanley, 1990; Therkelsen, 1993).

27 It is one of a family of sulfated galactans (Painter, 1983) with primary structures based
28 on a linear disaccharide repeating sequence of alternating 1,3 and 1,4-linked residues. The
29 other gelling carrageenan used commercially is iota. In both iota and kappa carrageenan the
30 1,4-linked residues occur predominantly as the 3,6-anhydride (Fig. 1), and the 1,3-linked
31 residues have a sulfate group at C(4). In nature, the anhydride bridge is absent in a significant
32 proportion of the 1,4-linked residues, but in commercial production structural regularity is
33 normally enhanced by treatment with alkali (Smidsrød, Larsen, Penas & Haug, 1967;
34 Stanley, 1963), giving structures close to the idealised repeating sequence in Fig. 1. Unlike
35 kappa carrageenan, iota has an additional sulfate substituent at C(2) of the 1,4-linked residue
36 (Anderson, Dolan & Rees, 1973). Thus iota carrageenan has two negative charges per
37 disaccharide, whereas kappa has only one.

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

43 Kappa carrageenan has a double helix structure similar to that of iota (Anderson,
44 Campbell, Harding, Rees & Samuel, 1969; Millane, Chandrasekaran, Arnott & Dea, 1988).
45 Again, gels form on cooling and melt on heating, but with substantial thermal hysteresis
46 (in marked contrast to the sol-gel and gel-sol transitions of iota). Hysteresis is attributed to
47 cation-induced aggregation of the kappa carrageenan double helices, with the aggregates
48 surviving to higher temperatures than those at which individual helices are formed on cooling
49 (Morris & Norton, 1983; Morris, Rees & Robinson, 1980). Some limited aggregation of
50 helices, with associated slight thermal hysteresis, may also occur for iota carrageenan in the
51 presence of high concentrations of Ca^{2+} cations (Goycoolea, Morris & Gidley, 1995; Tari,
52 Kara & Pekcan, 2010).

54 It has been demonstrated by NMR (Belton, Morris & Tanner, 1986; Grasdalen & Smidsrød,
55 1981; Piculell, Nilsson & Ström, 1989) that, unlike Li^+ and Na^+ , K^+ (and larger Group I
56 cations) bind to kappa carrageenan double helices. This reduces the net negative charge
57 on the helices, and promotes helix–helix aggregation by suppressing electrostatic repulsion.
58 Aggregation increases gel strength by giving an additional mechanism of crosslinking
59 (Viebeck, Piculell & Nilsson, 1994), and commercial kappa carrageenan is therefore normally
60 produced and supplied with K^+ as the predominant cation.

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

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

75 **2. Materials and methods**

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

80 Differential scanning calorimetry (DSC) measurements were made at a fixed carrageenan
81 concentration of 1.0 wt % (~25 mM w.r.t. sulfate groups) using a Setaram DSC III scanning
82 microcalorimeter at heating and cooling rates of $0.5^\circ\text{C}/\text{min}$. Water was used as thermal
83 reference, and sample and reference pans were balanced to within 0.05 mg (typical loading
84 ~850 mg).

85 Carrageenan was dissolved at 2.0 wt % by mechanical stirring at 80°C. Solutions of NaCl,
86 KCl and/or CaCl₂ were also prepared at twice the required concentration and mixed in equal
87 volumes with 2.0 wt % kappa carrageenan at 80°C, to give mixtures containing 1.0 wt %
88 polymer in the presence of the appropriate concentration of salt(s).

89 To take account of non-specific screening of electrostatic repulsion between carrageenan
90 helices, comparisons were made at equivalent values of ionic strength (with 1 mM CaCl₂
91 having the same ionic strength as 3 mM NaCl or KCl).

92 3. Results

93 Thermal hysteresis between the DSC exotherm arising from the disorder–order transition on
94 cooling and the endotherm from the order–disorder transition on heating is illustrated in Fig. 2
95 for 1.0 wt % Na⁺ kappa carrageenan in the presence of 100 mM KCl. The same general
96 pattern of a sharp exotherm and somewhat broader endotherm was observed for all
97 carrageenan–salt mixtures studied, but with large differences in the position of the DSC peaks
98 on varying concentration and type of salt.

99 Disorder–order and order–disorder transition temperatures can be conveniently characterised
100 by the temperature of maximum (absolute) heat flow in DSC (i.e. the temperature, T_{\max} , at
101 the top of the exotherms and bottom of the endotherms). As shown in Fig. 3, the effectiveness
102 of increasing concentrations of the three salts studied in raising T_{\max} values for 1.0 wt %
103 Na⁺ kappa carrageenan followed the order NaCl < CaCl₂ < KCl for both the disorder–order
104 transition on cooling (Fig. 3a) and the order–disorder transition on heating (Fig. 3b).

105 However, the extent of thermal hysteresis (Fig. 4) between the ordering and disordering
106 processes followed a different order: NaCl < KCl < CaCl₂. Greater thermal hysteresis with
107 CaCl₂ than with KCl is consistent with the proposal (Doyle et al., 2002) that Ca²⁺ cations
108 "cement" kappa carrageenan double helices together by binding between them in an
109 arrangement analogous to the "egg box" binding (Grant, Morris, Rees, Smith & Thom, 1973)
110 of Ca²⁺ between polyuronate sequences in calcium alginate and calcium pectinate gels,
111 whereas K⁺ acts indirectly by binding to individual helices and thus suppressing electrostatic
112 repulsion.

113 To explore the stability of Ca²⁺-induced aggregates of kappa carrageenan double helices
114 the effect of adding monovalent cations (Na⁺ and K⁺) was investigated. Two different
115 concentrations of Ca²⁺ were used in mixtures with 1.0 wt % Na⁺ kappa carrageenan: 12.5 mM
116 (stoichiometric) and 5 mM, and increasing concentrations of NaCl or KCl were added.

117 As shown in Fig. 5, as the concentration of KCl was raised the observed values of T_{\max} for
118 the disorder–order transition on cooling (Fig. 5a) and the order–disorder transition on heating
119 (Fig. 5b) increased from those observed with 12.5 or 5 mM Ca^{2+} alone towards the higher
120 values found (Fig. 3) with KCl, suggesting displacement of bound Ca^{2+} cations.

121 When the same experiment was repeated (Fig. 6) using NaCl instead of KCl, addition of
122 high concentrations of NaCl was found to cause a slight increase (Fig. 7a) in the temperature
123 of the disorder–order transition on cooling (Fig. 6a), which can be readily explained by
124 non-specific screening of electrostatic repulsion between the charged polymer coils, thus
125 facilitating intermolecular association into double helices.

126 In the heating direction (Fig. 6b), however, increasing concentrations of NaCl caused a
127 progressive reduction in T_{\max} for the disorder–disorder transition, towards the lower
128 values observed (Fig. 3) for NaCl alone. In consequence, addition of high concentrations
129 of NaCl had the surprising effect of *lowering* the transition temperature (Fig. 7b), rather than
130 giving the increase in T_{\max} that would be expected from the general behaviour of charged
131 polysaccharides.

132 **4. Discussion and conclusions**

133 The obvious interpretation of the results presented in Figs. 5 - 7 is that progressive addition
134 of KCl or NaCl causes progressive displacement of Ca^{2+} cations bound between kappa
135 carrageenan double helices, with the overall behaviour then approaching that observed
136 (Fig. 3) for the same concentrations of the monovalent cations in the absence of Ca^{2+} . The
137 outcome is an increase in thermal stability of the helix–helix aggregates on addition of KCl
138 and a reduction with NaCl, which leads to the unusual (perhaps unprecedented) observation
139 that addition of NaCl lowers the temperature of the order–disorder transition (Fig. 7b).

140 The ability of monovalent cations to displace Ca^{2+} is, in itself, further evidence of site-binding
141 of calcium ions to kappa carrageenan double helices (if they weren't bound they could not be
142 displaced), and reinforces the conclusion from greater thermal hysteresis with Ca^{2+} than with
143 K^+ (Fig. 4) and maximum in gel strength at stoichiometric equivalence of Ca^{2+} to sulfate
144 groups of the polymer (Doyle et al., 2002) that calcium ions bind *between* the double helices,
145 rather than to individual helices.

147 The ability of monovalent salts to displace Ca^{2+} cations bound to anionic polysaccharides
148 has been demonstrated previously for calcium alginate (Morris, Rees, Thom & Boyd, 1978)
149 and calcium pectinate (Morris, Powell, Gidley & Rees, 1982). Both of these form "egg box"
150 structures (Grant et al., 1973) in which calcium ions are sandwiched in site-bound arrays
151 between 2-fold (zig-zag) sequences of polyguluronate (from alginate) or polygalacturonate
152 from pectin. On addition of increasing concentrations of monovalent cations (Na^+ or Me_4N^+),
153 the amount of bound Ca^{2+} dropped from around stoichiometric equivalence to the carboxylate
154 groups of the polyuronate sequences to 50% stoichiometric, indicating a highly stable dimeric
155 structure with a single array of calcium ions bound between two polysaccharide chains, with
156 only the inner faces of the 2-fold ordered structures participating in binding.

157 Displacement of Ca^{2+} cations bound between (but not within) "egg box" dimers suggests
158 a parallel with similar displacement from between the dimers (double helices) of kappa
159 carrageenan.

160 **Acknowledgements**

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163 commercial, or not-for-profit sectors.

165 **References**

- 166 Anderson, N.S., Campbell, J.W., Harding, M.M., Rees, D.A., & Samuel, J.W.B. (1969).
167 X-ray diffraction studies of polysaccharide sulphates: double helix models for κ - and ι -
168 carrageenans. *Journal of Molecular Biology*, 45, 85-99.
- 169 Anderson, N.S., Dolan, T.C.S., & Rees, D.A. (1973). Carrageenans. Part VII. Polysaccharides
170 from *Eucheuma spinosum* and *Eucheuma cottonii*. The covalent structure of ι -carrageenan.
171 *Journal of the Chemical Society, Perkin Transactions I*, 2173-2176.
- 172 Arnott, S., Scott, W.E., Rees, D.A., & McNab, C.G.A. (1974). ι -Carrageenan: molecular
173 structure and packing of polysaccharide double helices in oriented fibres of divalent cation
174 salts. *Journal of Molecular Biology*, 90, 253-267.
- 175 Belton, P.S., Morris, V.J., & Tanner, S.F. (1986). ^{39}K and ^{87}Rb NMR study of chemical shift
176 effects in ι - and κ -carrageenan gels. *Macromolecules*, 19, 1618-1621.
- 177 Doyle, J., Giannouli, P., Philp, K., & Morris, E.R. (2002). Effect of K^+ and Ca^{2+}
178 cations on gelation of κ -carrageenan. In P.A. Williams & G.O. Phillips (Eds.),
179 *Gums and stabilisers for the food industry 11* (pp. 158-164). Cambridge, UK:
180 Royal Society of Chemistry.
- 181 Doyle, J., Giannouli, P., Richardson, R.K., & Morris, E.R. (2018). Site binding
182 of cations between double helices in Ca^{2+} -induced gelation of κ -carrageenan.
183 *Food Hydrocolloids*, in preparation.
- 184 Glicksman, M. (1983). Red seaweed extracts (agar, carrageenans, furcellaran).
185 In M. Glicksman (Ed), *Food Hydrocolloids*, Vol. 2 (pp. 73-113). Boca Raton, FL:
186 CRC Press.
- 187 Goycoolea, F.M., Morris, E.R., & Gidley, M.J. (1995). Screening for synergistic interactions
188 in dilute polysaccharide solutions. *Carbohydrate Polymers*, 28, 351-358.
- 189 Grant, G.T., Morris, E.R., Rees, D.A., Smith, P.J.C., & Thom, D. (1973). Biological
190 interactions between polysaccharides and divalent cations: the egg-box model.
191 *FEBS Letters*, 32, 195-198.
- 192 Grasdalen, H., & Smidsrød, O. (1981). ^{133}Cs NMR in the sol-gel states of aqueous carrageenan.
193 Selective site binding of cesium and potassium ions in κ -carrageenan gels. *Macromolecules*,
194 14, 229-231.

- 195 Millane, R.P., Chandrasekaran, R., Arnott, S., & Dea, I.C.M. (1988).
196 The molecular structure of kappa-carrageenan and comparison with iota carrageenan.
197 *Carbohydrate Research*, 182, 1-17.
- 198 Morris, E.R., & Norton, I.T. (1983). Polysaccharide aggregation in solutions and gels.
199 In E. Wyn-Jones & J. Gormally (Eds.), *Aggregation processes in solution*,
200 (pp. 549-593). Amsterdam: Elsevier.
- 201 Morris, E.R., Powell, D.A., Gidley, M.J., & Rees, D.A. (1982). Conformations and
202 interactions of pectins. I. Polymorphism between gel and solid states of calcium
203 polygalacturonate. *Journal of Molecular Biology*, 155, 507-516.
- 204 Morris, E.R., Rees, D.A., & Robinson, G. (1980). Cation-specific aggregation of carrageenan
205 helices: domain model of polymer gel structure. *Journal of Molecular Biology*, 138, 349-362.
- 206 Morris, E.R., Rees, D.A., Thom, D., & Boyd, J. (1978). Chiroptical and stoichiometric
207 evidence of a specific, primary dimerisation process in alginate gelation. *Carbohydrate*
208 *Research*, 66, 145-154.
- 209 Painter, T.J. (1983). Algal polysaccharides. In G.O. Aspinall (Ed.), *The polysaccharides*, Vol. 2
210 (pp. 195-285). New York: Academic Press.
- 211 Piculell, L. (1995). Gelling carrageenans. In A.M. Stephen (Ed.), *Food polysaccharides and*
212 *their applications* (pp. 205-244). New York: Marcel Dekker.
- 213 Piculell, L., Nilsson, S., & Ström, P. (1989). On the specificity of the binding of cations to
214 carrageenans: counterion N.M.R. spectroscopy in mixed carrageenan systems *Carbohydrate*
215 *Research*, 188, 121-135.
- 216 Rees, D.A. (1970). A double helix structure in food. *Science Journal*, 6, 47-51.
- 217 Smidsrød, O., Larsen, B., Pernas, A.J., & Haug, A. (1967). The effect of alkali treatment on
218 the chemical heterogeneity and physical properties of some carrageenans. *Acta Chemica*
219 *Scandinavica*, 21, 2585-2598.
- 220 Stanley, N.F. (1963). Process for treating a polysaccharide of seaweeds of
221 the Gigartinaceae and Solieriaceae families. *US Patent* 3 094 517.
- 222 Stanley, N.F. (1990). Carrageenans. In P. Harris (Ed.), *Food gels* (pp. 79-119).
223 Barking, UK: Elsevier Science Publishers.

- 224 Tari, Ö, Kara, S., & Pekcan, Ö (2010). Thermal phase transitions of iota carrageenan in CaCl₂
225 solutions: A fluorescence study. *Journal of Macromolecular Science, Part B: Physics*, 50,
226 306-318.
- 227 Therkelsen, G.H. (1993). Carrageenan. In R.L. Whistler & J.N. BeMiller (Eds.), *Industrial*
228 *gums*, Third Edition (pp. 145-180). San Diego, CA: Academic Press.
- 229 Viebke, C., Piculell, L., & Nilsson, S. (1994). On the mechanism of gelation of
230 helix-forming biopolymers. *Macromolecules*, 27, 4160-4166.

232 **Legends to figures**

233

234 **Fig. 1.** Idealised disaccharide repeating structure of gelling carrageenans. R = H in kappa
235 and SO₃⁻ in iota.

236

237 **Fig. 2.** DSC traces recorded on cooling and heating at 0.5°C/min for 1.0 wt % Na⁺ kappa
238 carrageenan with 100 mM added KCl.

239

240 **Fig. 3.** Effect of ionic strength on peak-maximum temperature (T_{max}) for 1.0 wt % Na⁺ kappa
241 carrageenan on (a) cooling and (b) heating in the presence of increasing concentrations of
242 NaCl (▲), KCl (■) or CaCl₂ (●).

243

244 **Fig. 4.** Effect of ionic strength on the extent of thermal hysteresis between DSC cooling and
245 heating scans (Fig. 3) for 1.0 wt % Na⁺ kappa carrageenan in the presence of increasing
246 concentrations of NaCl (▲), KCl (■) or CaCl₂ (●).

247

248 **Fig. 5.** Variation of peak-maximum temperature with ionic strength on addition of increasing
249 concentrations of KCl to 1.0 wt % Na⁺ kappa carrageenan in mixtures with 5 mM (●) or
250 12.5 mM (▲) CaCl₂ on (a) cooling and (b) heating The corresponding values from addition
251 of KCl (□) or CaCl₂ (○) alone (Fig. 3) are shown for comparison.

252

253 **Fig. 6.** Variation of peak-maximum temperature with ionic strength on addition of increasing
254 concentrations of NaCl to 1.0 wt % Na⁺ kappa carrageenan in mixtures with 5 mM (●) or
255 12.5 mM (▲) CaCl₂ on (a) cooling and (b) heating The corresponding values from addition of
256 NaCl (Δ) or CaCl₂ (○) alone (Fig. 3) are shown for comparison.

257

258 **Fig. 7.** DSC traces recorded on (a) cooling and (b) heating for 1.0 wt % Na⁺ kappa
259 carrageenan with 12.5 mM CaCl₂ in the presence (solid line) or absence (dashed line)
260 of 100 mM NaCl.

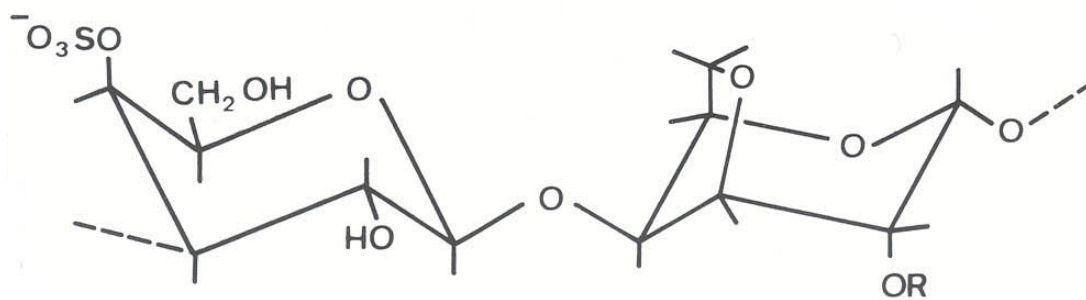


Fig. 1. Idealised disaccharide repeating structure of gelling carrageenans. R = H in kappa and SO_3^- in iota.

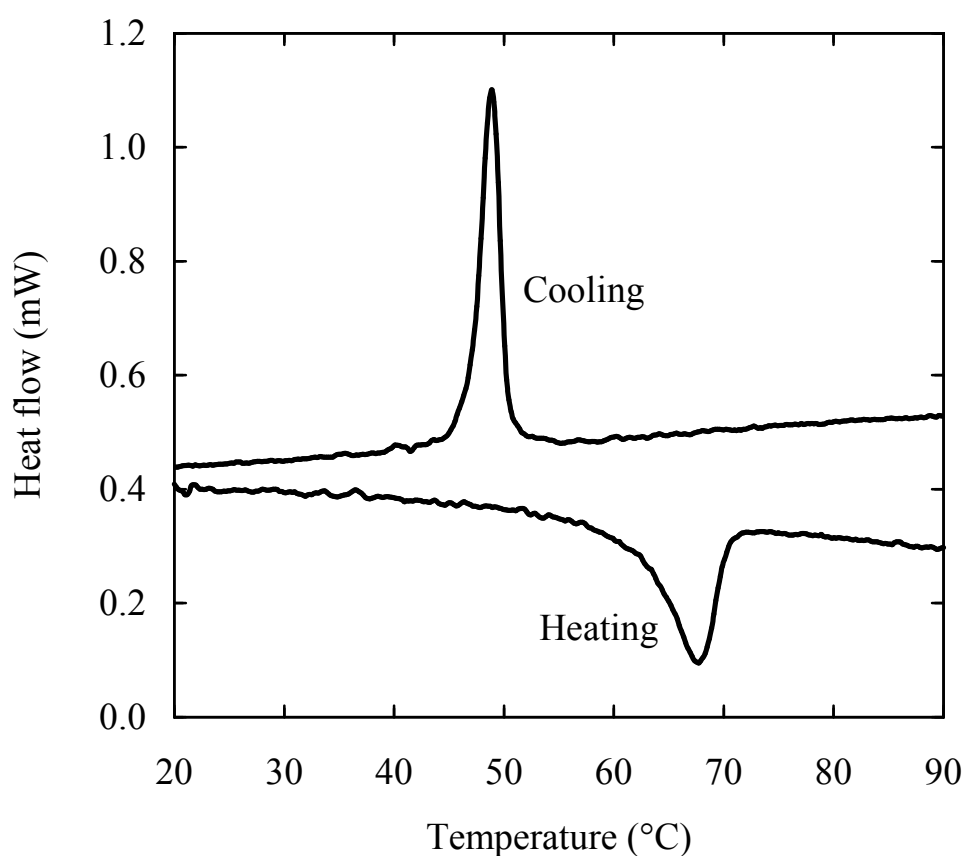


Fig. 2. DSC traces recorded on cooling and heating at $0.5^\circ\text{C}/\text{min}$ for 1.0 wt % Na^+ kappa carrageenan with 100 mM added KCl.

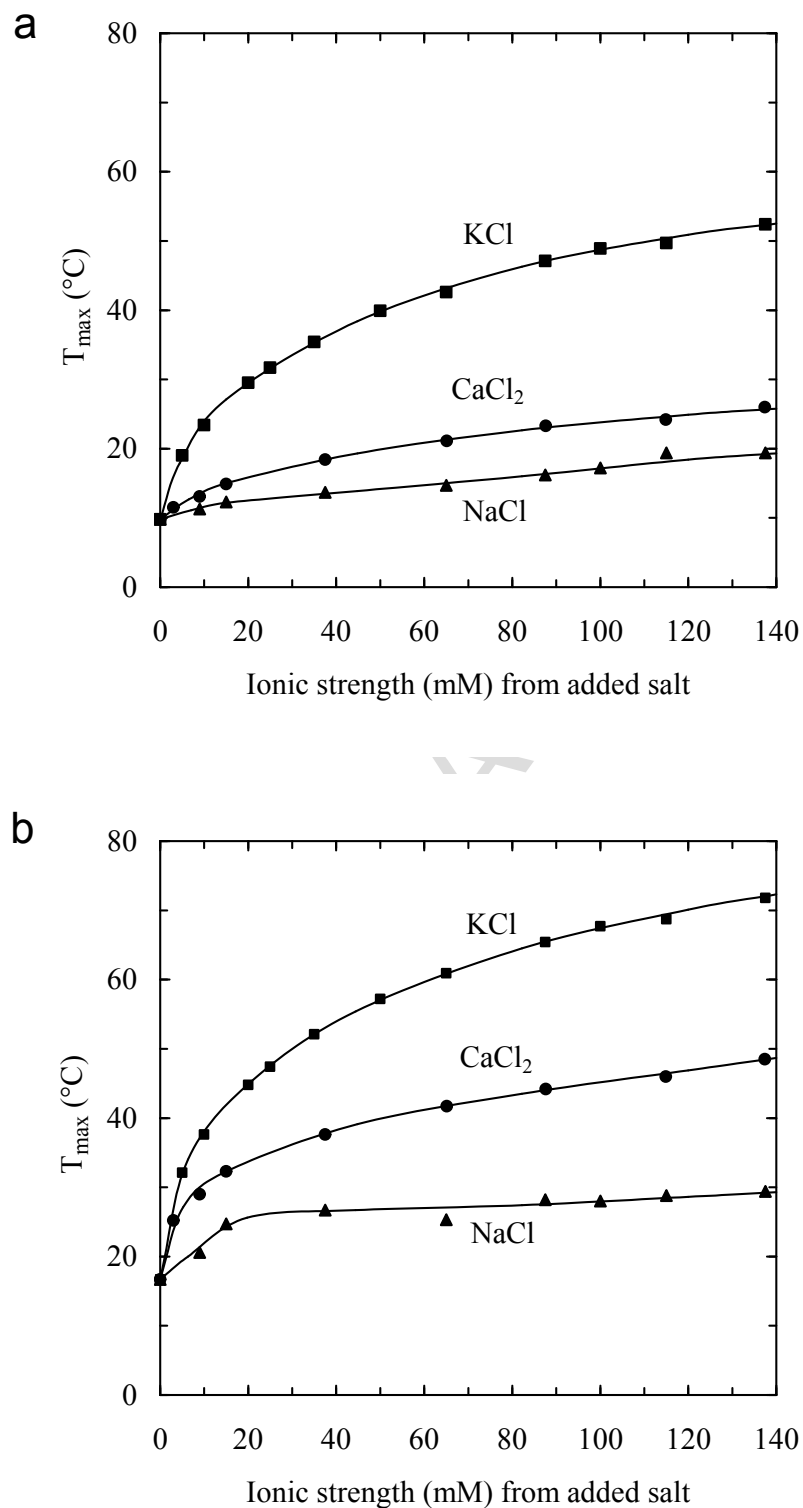


Fig. 3. Effect of ionic strength on peak-maximum temperature (T_{\max}) for 1.0 wt % Na⁺ kappa carrageenan on (a) cooling and (b) heating in the presence of increasing concentrations of NaCl (\blacktriangle), KCl (\blacksquare) or CaCl₂ (\bullet).

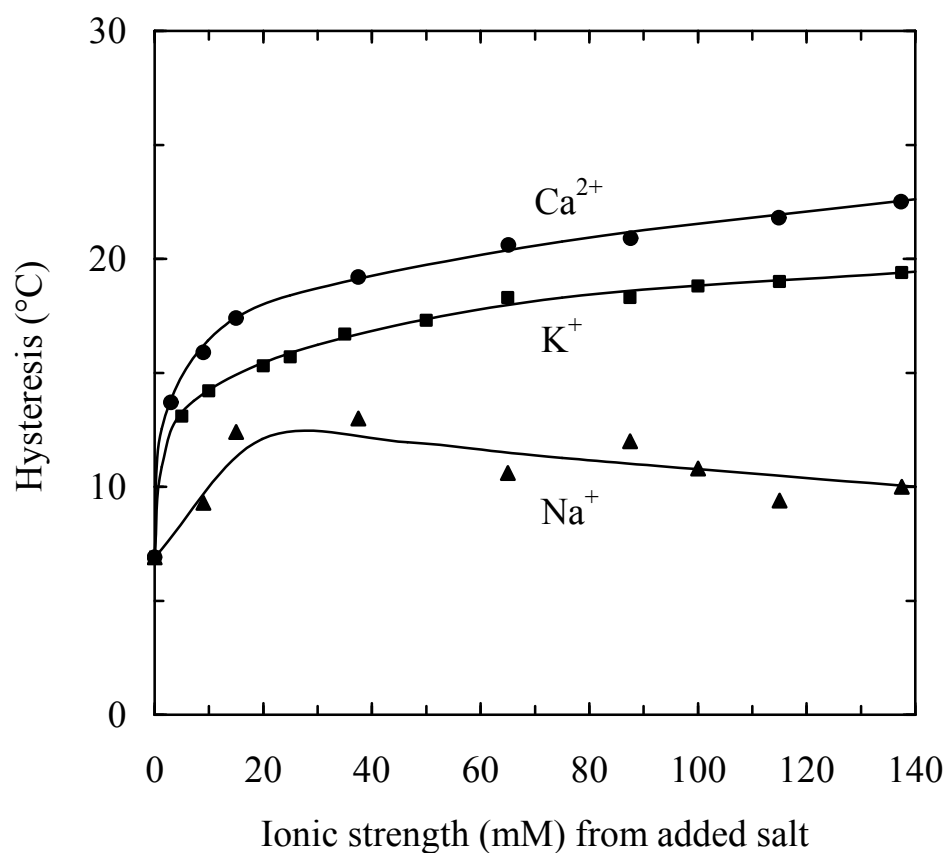


Fig. 4. Effect of ionic strength on the extent of thermal hysteresis between DSC cooling and heating scans (Fig. 3) for 1.0 wt % Na⁺ kappa carrageenan in the presence of increasing concentrations of NaCl (▲), KCl (■) or CaCl₂ (●).

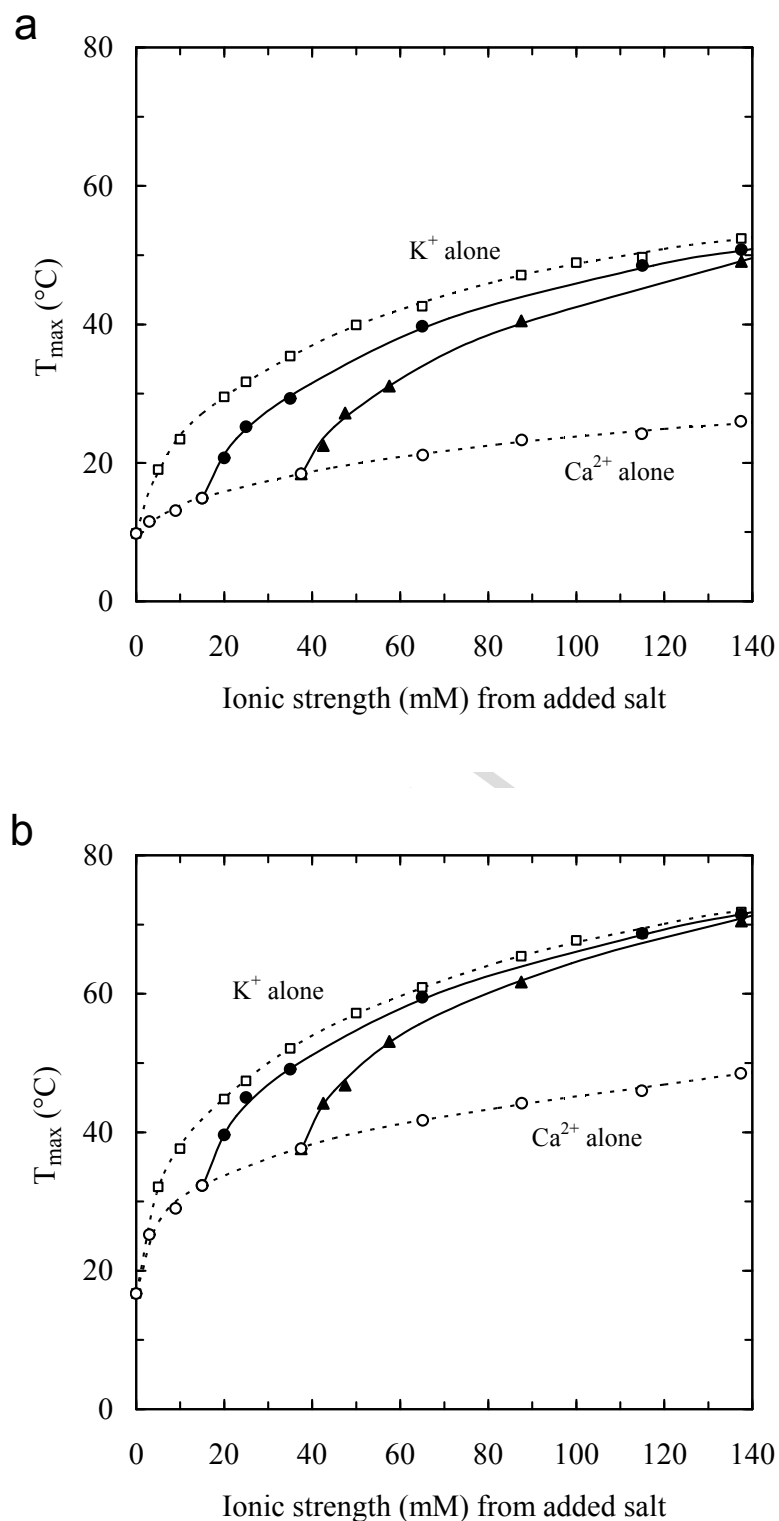


Fig. 5. Variation of peak-maximum temperature with ionic strength on addition of increasing concentrations of KCl to 1.0 wt % Na⁺ kappa carrageenan in mixtures with 5 mM (●) or 12.5 mM (▲) CaCl₂ on (a) cooling and (b) heating. The corresponding values from addition of KCl (□) or CaCl₂ (○) alone (Fig. 3) are shown for comparison.

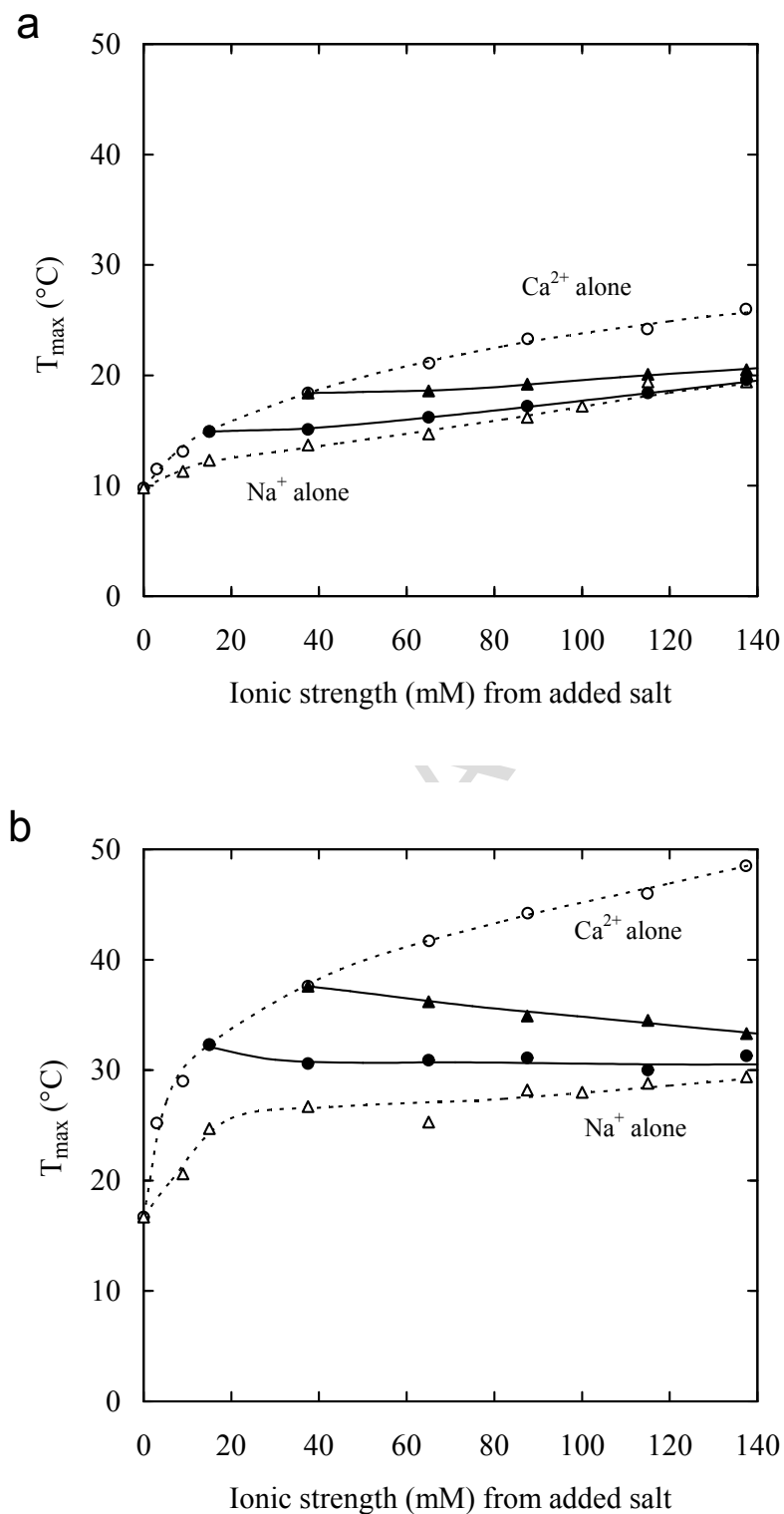


Fig. 6. Variation of peak-maximum temperature with ionic strength on addition of increasing concentrations of NaCl to 1.0 wt % Na⁺ kappa carrageenan in mixtures with 5 mM (●) or 12.5 mM (▲) CaCl₂ on (a) cooling and (b) heating. The corresponding values from addition of NaCl (Δ) or CaCl₂ (○) alone (Fig. 3) are shown for comparison.

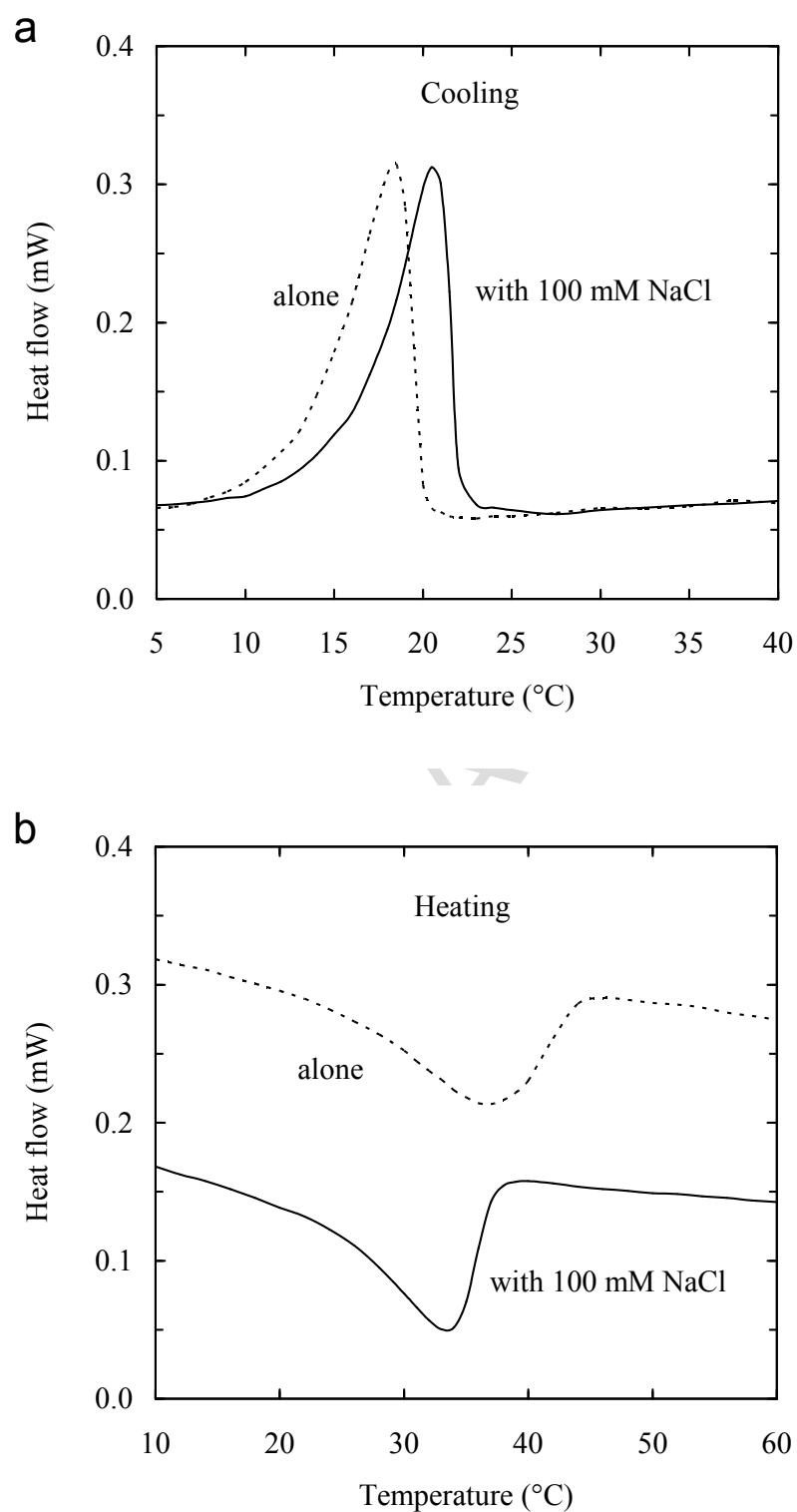


Fig. 7. DSC traces recorded on (a) cooling and (b) heating for 1.0 wt % Na⁺ kappa carrageenan with 12.5 mM CaCl₂ in the presence (solid line) or absence (dashed line) of 100 mM NaCl.

Highlights

- Site-binding of calcium cations between kappa carrageenan double helices
- Consequent large hysteresis between ordering and disordering transitions in DSC
- Bound Ca^{2+} displaced progressively by increasing concentrations of NaCl or KCl
- KCl moves order–disorder transition towards higher temperatures seen with K^+ alone
- High concentrations of NaCl *lower* transition temperature rather than raising it