Specific Ion Effects in ι-Carrageenate Gels

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Summary Measurements of rigidity moduli and ^{39}K and ^{23}Na n.m.r. have been used to investigate the roles played by the cations calcium, potassium, and sodium in ι-carrageenate gels.

THE influence of cations on the structure of anionic polysaccharide gels is of both academic and technological importance.[1] Samples of ι-carrageenate contain principally calcium, potassium, and sodium cations. Until recently[2,3] little data has been available on samples in which the absolute ion concentrations were specified and there has been no previous direct observation of the binding of specific ions. In this study of pure samples of calcium, potassium, and sodium ι-carrageenate we demonstrate the effects of the 3 ions on the bulk rheological properties and, *via* n.m.r., illustrate differences in the binding of sodium and potassium in these gels.

The monovalent ions Na^+ and K^+ may be removed by ion exchange at room temperature. Exchange of calcium was carried out at 90°C. Rigidity modulus (G_R) measurements on sodium, potassium, and calcium gels are shown in Figure 1. The data were obtained by the modification of the Saunders and Ward method[4] suggested by Scott–Blair and Burnett.[5] Sodium gels would only sustain low applied-pressures suggesting a low yield-point which is consistent with recently reported data.[2,3] Figure 1 clearly demonstrates that for a

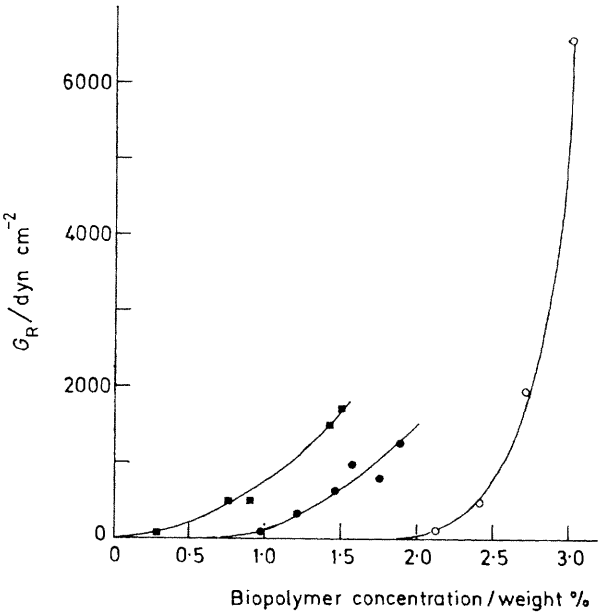

FIGURE 1. Rigidity modulus (G_R) *vs.* biopolymer concentration for calcium (■), potassium (●), and sodium (○) ι-carrageenate. Cation concentrations are expressed as mass of cation per mass of biopolymer. Calcium ι-carrageenate (5% Ca), potassium ι-carrageenate (10·5% K), and sodium ι-carrageenate (9% Na).

given biopolymer concentration G_R is largest for calcium gels and larger for potassium than for sodium gels.

We have used n.m.r. spectroscopy to explore the roles of different cations on the gel structure. Calcium spectra are difficult to obtain but Figure 2 illustrates the different binding of sodium and potassium. The line width of the ^{23}Na peak, together with T_1 relaxation data, is consistent with the mobilities of sodium ions in sodium chloride solutions.[6] The ^{39}K peak is reminiscent of the type of resonance observed in powder samples. The spectrum should be a triplet and the absence of the two additional peaks is probably because they are considerably displaced from the central line. The width of the peak (8·5 kHz) clearly demonstrates the restricted mobility of potassium in the gel. ^{39}K N.m.r. spectra for potassium chloride solutions are typically a few Hz in width.[6] The assymmetry of the ^{39}K resonance arises from an anisotropic chemical-shift tensor and this is consistent with the proposed domain model for carrageenan gels.[2,3] However, this data does not, in itself, confirm this model since spectra have not been obtained on non-gelling concentrations of potassium ι-carrageenate.

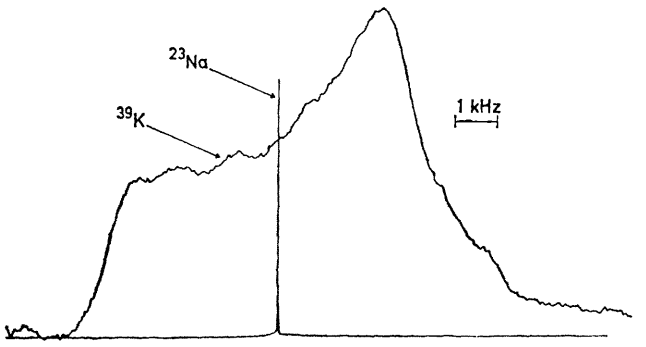

FIGURE 2. ^{39}K and ^{23}Na n.m.r. spectra for potassium (K 10·5%, polymer 2%) and sodium (Na 9%, polymer 2·7%) ι-carrageenate gels, respectively, obtained using a Bruker CXP200 at room temperature. Operating conditions were: ^{39}K 9·36 MHz, 115561 scans, repetition time 0·5 s; ^{23}Na 529 MHz, 250 scans, repetition time 1 s. Ion concentrations are expressed as mass of cation per mass of biopolymers.

In conclusion, we have observed differences in the binding of calcium, sodium, and potassium in ι-carrageenate gels. This is reflected in the bulk rheological properties of the gels. N.m.r. provides the first *direct* evidence of differences in the binding of sodium and potassium.

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