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ISO-IONIC AND ISO-THERMAL PHASE TRANSITIONS IN IONIC POLYSACCHARIDES: A CALORIMETRIC STUDY.

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ABSTRACT

The process of conformational transition of κ-carrageenan in aqueous solution containing cesium chloride was studied by microcalorimetry. The experimental evidence as well as the comparison of data collected with the prediction of Manning's theoretical model, suggests that the transition occurs by a two-step mechanism.

INTRODUCTION

κ-carrageenan is an algal polysaccharide composed of linear chains of alternating 1,3-linked β-$\underline{\underline{D}}$-galactopyranose residues, most of which are sulfated on position 4, and 1,4-linked α-$\underline{\underline{D}}$-galactopyranose residues, most of which are present as 3,6-anhydride. Experimental evidence shows that the gelation of κ-carrageenan in aqueous solution containing monovalent cations is a complex process. Ordering and aggregation of chains occur. However, in spite of many data so far collected, it is not understood whether the two phenomena are simultaneous or occur in different steps (ref.1,2). We have investigated this process by differential scanning microcalorimetry, DSC (in iso-ionic mode) and mixing microcalorimetry (in iso-thermal mode), and have then compared our data with the predictions of a simple model, which consists of a coil-single helix transition followed by side-by-side dimerisation of the helices by cation-selective salt-bridge formation (ref.3).

EXPERIMENTAL

Isothermal measurements were performed on a LKB 10700-2 batch-type microcalorimeter equipped with gold cells. Data were collected at 10° and 25°C. Instrumental uncertainties were found to be within 1% of the experimental values. DSC measurements were carried out on a Setaram Bio-DSC microcalorimeter. The temperature range explored was from 10°C up to 15 degrees above the temperature of transition. The solutions were maintained at least 1 hour at low temperature before each heating-cooling cycle. Scanning rate was 0.2 or 0.5°C/min; higher rates were found to affect the shape of the peak. The instrumental uncertainty of the Bio-DSC microcalorimeter is 0.5%.

RESULTS AND DISCUSSION

The ΔH values of mixing of tetramethylammonium κ-carrageenate with CsCl solutions, corrected for the heats of dilution of both polymer and salt, are reported in Fig.1 as a function of the ionic strength, I, which was computed including the contribution of the polyelectrolyte. The curve at 10°C clearly indicates a two-step process (in the considered model, disorder-order transition and aggregation, respectively). The curve at 25°C shows the same features, although here the resolution of the two inflections is less evident. In both cases, the ΔH is about -8 kJ/monomol for the first transition and about -18 kJ/monomol for the overall process. The values of I corresponding to the midpoints of the first inflections of the two curves are reported in Fig.2 with the values of the temperatures (triangles). The plots of logI vs. 1/T reported in Fig.2 for a κ-carrageenan solution containing a uni-univalent salt can be considered as a phase diagram, where I is a parameter directly linked to the relative stability of the different conformations of the polymer in solution. Two straight lines, drawn through data points obtained by various techniques, whose slopes are -3500 and -2600 K respectively, show four regions in which the following conformations appear to predominate (ref.3): I) disordered chains (rc); II) dimers of single helices (1h.1h); III) single helices (1h) + 1h.1h; IV) 1h + rc. The shapes of the heating thermograms reveal a multistep transition (disaggregation, order-disorder transition). They depend on I, on the scanning rate, and on the thermal story of the sample

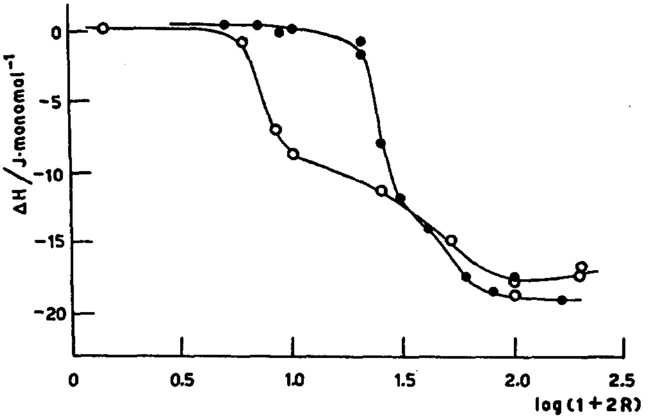

Fig.1. Enthalpy of mixing of tetramethylammonium κ-carrageenate with CsCl solution as a function of the final ionic strength of the solution, I.

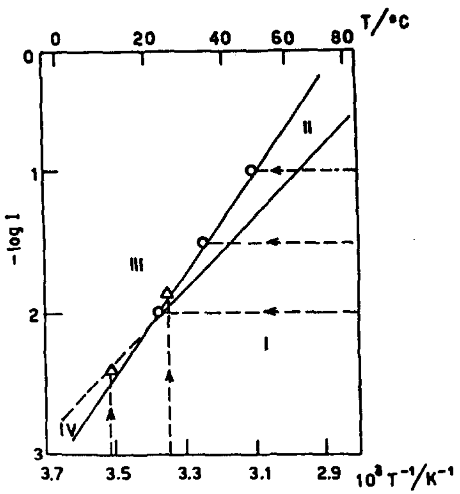

Fig.2. Phase diagram of κ-carrageenan in aqueous solution of uni-univalent salts.

(i.e., the residence time at low temperature and the number of heating and cooling cycles). Cooling thermograms constantly show a single peak. No differences in ΔH were detected between heating and cooling thermograms. The values of the temperature of transition corresponding to the maxima of cooling curves are reported in Fig.2 (circles). Both isothermal and iso-ionic data agree with DSC data existing in the literature (ref.4-6). Typical DSC thermograms are reported in Fig.3.

The data of ΔH of transition obtained by these two techniques are not identical, because of the differences in the apparent heat capacity and in the temperature dependence of the heat of mixing.

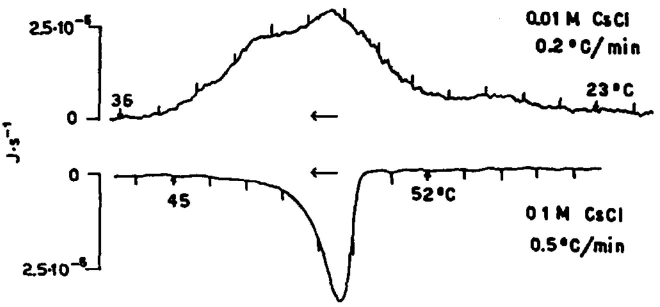

Fig.3. Typical DSC thermograms of κ-carrageenan in the presence of Cs^+ cations. Polymer concentration, 1 g/L.

COMPARISON WITH THEORY AND CONCLUSION

For a polyelectrolyte which undergoes a cooperative conformational transition induced by temperature and/or ionic strength, the theory predicts a linear relationship between logI and 1/T, as long as the ΔH of transition is independent of I (ref.7,8). The proportionality depends exclusively on the values of the initial and final linear charge density parameters (ξ_i and ξ_f respectively,with ξ defined as $\xi = e^2/DkTb$, where e is the elementary charge, D is the dielectric constant of the bulk medium, k is the Boltzmann constant, T is the absolute temperature, and b is the average spacing of charged groups along the axis length). In order to compare the theoretical values of ΔH of transition with the experimental ΔH from mixing data, the latter ones were corrected for the electrostatic contribution accompanying the mixing of a polyelectrolyte with a uni-univalent salt (ref.8). The experimental values of ΔH for the first step and the whole process (-8 and -18 kJ/monomol, respectively) are in agreement with the values predicted by the Manning's theory for the formation of a single helix from a coil and for the formation of dimers of single helices. The calculated values of the two processes are -6 and -18 kJ/monomol, respectively, using b = 10.3, 8.4, and 4.2 Å in the case of rc, 1h, and 1h.1h, respectively.

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