Macromol. Symp. **186,** *141–146 (2002)*

Metal Ion – Ionic Polysaccharide Interactions: Theoretical Developments And Experimental Results

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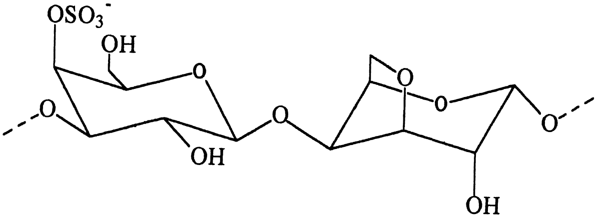
Summary: A modification of the Counterion Condensation (CC) theory of linear polyelectrolytes has been developed to take into account the presence of specific interactions between the polymer and the counterions. The particular case in which the polymer is the Ionic Polysaccharide (IPS) κ-carrageenan and the ions are monovalent alkaline ions with high atomic number (*e.g.* K^+, Cs^+) has been considered. κ-carrageenan in the presence of such ions undergoes a conformational transition eventually leading to the formation of side-by-side ordered pairs of chains, acting as junctions in a 3-D gel network. The presence of the conformational equilibrium leading to the fundamental ordered single chain (1h) and of the following one leading to chain pairing (1h.1h) complicates the description of the overall process. Nevertheless, they have been successfully accommodated together with the specific ion-polymer interactions to give a self-consistent set of thermodynamic equations. The application of the model to the experimental calorimetric data of mixing κ-carrageenan with Cs^+ ions has been successful. The thermodynamic parameters for the main chain conformational changes, as well as those for the specific interactions, have been calculated. In addition, the approach allowed for the evaluation of the number of polymer repeating units in the cooperative units of both 1h and of 1h.1h. They are as large as 50 and 35, respectively.

Introduction

Ionic Polysaccharides (IPS) exhibit interesting physical chemical properties like, *e.g.*, the ability to give rise to gels that render them of the utmost interest for the food and the biomedical industry. The stability of those structure results from the interplay of different effects: long range electrostatic interactions, conformational aspects and specific interactions with metal ions. IPS are usually rather elongated linear chains that ideally lend themselves to be treated as linear polyelectrolytes. The Counterion condensation (CC) theory of linear polyelectrolytes [1] is a simple and handy theoretical tool that already proved to be successful in describing the physical chemical behavior of, *e.g.*, DNA. [2] Moreover, it proved to be flexible enough to be modified to encompass

CCC 1022-1360/00/$ 17.50+.50/0

more sophisticated aspects like chain flexibility [3] and the description of systems of counterions of mixed valence. [4] For all that it was decided to include more specific metal ion / polymer interactions in systems undergoing ion-induced conformational changes. The modified theory was tested in the case of the IPS κ-carrageenan (KC, **1**).



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KC is a sulfated galactan that is known to give rise to thermoreversible gels, particularly so in the presence of monovalent metal ions (counterions) of high atomic number (*Me^+*: K^+, Rb^+, Cs^+). [5] Intramolecular chain ordering, followed by lateral association of the ordered single helices (*1h*), is known to be the prerequisite for gel formation by KC in aqueous media, [6-8] according to the scheme: *d* (disordered conformation) → *1h* → *1h.1h.*

The final goal of this work is to produce a reliable description of the free energy of each of the various states involved in the metal-mediated process. It can be achieved by factorizing the problem into different parts: *i)* the identification of the correct geometrical parameters of the conformations involved, with the corresponding values of the linear charge density parameters; *ii)* the role of the ionic-strength dependent part of the transition free energy (ΔG_{tr}) of polyelectrolytic nature *vs.* the non-ionic ΔG_{tr}; *iii)* the formulation of the free-energy terms of the metal-polymer specific interaction in relation to the peculiar state of the counterions *condensed* around the IPS.

Results and Discussion

The CC theory enables one to calculate the ΔH_{tr} from the slope of the linear conformational phase diagram (- log I *vs.* T_m^{-1}), knowing the average values for the projections on the chain axis of the distance between the charges, b, for each conformation, and given a certain value of the dielectric constant, D, of the solvent: [7,9]

$$\Delta H_{tr} / [-d \log I / d T_m^{-1}] = (\text{constant} / D) [1/(b_{1h}) - 1/(b_{disord})] \quad (1)$$

For the fundamental conformational transition (*d → 1h*, see Figure 1), no specific, localized interaction occurs for solvents (water – W, formamide – FA) where condensation of counterions does not take place. Difference between monovalent counterions can be easily traced back to bulk average properties of the solvent. For DMSO condensation takes place and the thermodynamic terms for the specific metal-polymer interactions can be well estimated. Interestingly enough, however, the calculated enthalpic and entropic contributions of the non-ionic component of ΔG_{tr} for W, FA and DMSO nicely follow a Barclay-Butler type of relationship (Table 1).

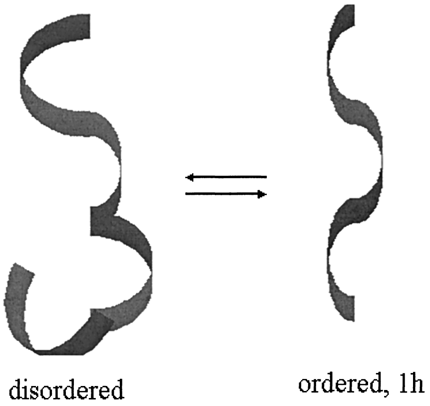

Figure 1. Schematic representation of the intramolecular conformational transition of κ-carrageenan.

Table 1. Thermodynamic parameters for the non-ionic component of the intramolecular conformational transition of κ-carrageenan.

solvent	Dielectric constant	$\Delta H^{n.pol.}$ J mol^{-1}	$\Delta S^{n.pol.}$ J K^{-1} mol^{-1}	$\Delta H^{n.pol.} / \Delta S^{n.pol.}$ K
DMSO	46.83	-7903	-21.81	362
Water	78.54	-5638	-15.75	358
Formamide	108.9	-5176	-14.48	357

Aqueous gel formation requires the lateral alignment of ordered stretches in the *1h.1h* conformation. The corresponding linear charge density implies the condensation of counterions. This process enhances the specific interactions between the IPS chain and the gel-inducing monovalent counterion. The latter is shown to be strongly favored both by enthalpy and entropy (see last two rows of Table 2). Also in this case the slope of the conformational phase diagram allows one to calculate the thermodynamic parameters for the transition (last column of Table 2).

Table 2. Calculated thermodynamic values for the *dis → 1h* and for the *dis → 1h.1h* conformational transitions of κ-carrageenan in aqueous CsCl solutions. Values in columns 2-4, and 5 pertain to different calculation procedures (see text).

	Isothermal			***Log I vs. 1/T***
	T = 283.15 K	T = 298.15 K	T = 308.15 K	
$(\Delta H^{n.pol.})_{dis \rightarrow 1h}$ kJ mol^{-1}	-5.64	-5.64	-5.64	-5.64
$(\Delta S^{n.pol.})_{dis \rightarrow 1h}$ J mol^{-1} K^{-1}	-15.8	-15.8	-15.8	-15.8
Size of the cooperative unit, n	50	50	50	-
$(\Delta H^{n.pol.})_{dis \rightarrow 1h.1h}$ kJ mol^{-1}	-18.62	-18.77	-18.77	-18.57±0.19
$(\Delta S^{n.pol.})_{dis \rightarrow 1h.1h}$ J mol^{-1} K^{-1}	-47.7	-47.7	-47.7	-48.1±0.5
Size of the cooperative unit, 2m	34	36	34	-
(ΔH^{aff}) kJ mol^{-1}	-3.31	-3.31	-3.31	-3.33
(ΔS^{aff}) J mol^{-1} K^{-1}	2.5	2.5	2.5	5.4±2.1

Experimental data of the heat of transition (see Figure 2) not only are the basis for the calculation of the thermodynamic parameters: their dependence on the concentration of added Me^{+} provides the information for the evaluation of the cooperativity of the *d→1h* and of the *1h→1h.1h* transitions (see Table 2). Separate fitting to the curves obtained at different temperatures according to the very general scheme:

$$\Delta H^{exp} = x_{1h} \; (\Delta H^{np})_{1h} + x_{1h.1h} (\Delta H^{np})_{1h.1h} + r_{1h.1h} \, (x_{1h.1h}) \, \Delta H^{aff} \qquad (2)$$

Where $r_{1h.1h}$ is the fraction of condensed counterions in the 1h.1h conformation. The general positions have been used, also for the calculation of the mole fraction of the different species, x_i:

$$\Delta G^{\text{tot}}(I, T) = \Delta G^{\text{pol}} + \Delta G^{\text{n.pol}} + \Delta G^{\text{aff}} \tag{3}$$

$$\Delta G^{\text{pol}} = \Delta G^{\text{el}} \ [+ \Delta G^{\text{cond}} + \Delta G^{\text{free}} + \Delta G^{\text{solvent}}] \tag{4}$$

$$\Delta G^{\text{n.pol}} = [\Delta H^{\text{n.pol}} - T\,\Delta S^{\text{n.pol}}] \tag{5}$$

$$\begin{aligned}\Delta G^{\text{aff}} &= r_{\text{lh.lh}}\,((\Delta G^{\text{aff}})^{\circ})_{\text{lh.lh}} \\ &= r_{\text{lh.lh}}\,[(\Delta H^{\text{aff}})_{\text{lh.lh}} - T\,(\Delta S^{\text{aff}})_{\text{lh.lh}}]\end{aligned} \tag{6}$$

The agreement between the values calculated at different temperatures, and between those and the values calculated from the phase diagram is excellent. It gives confidence in the used method and in the conformational assumptions therein involved.

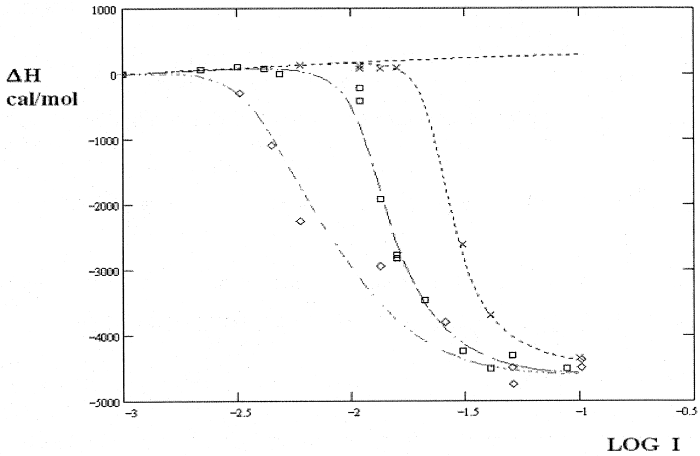

Figure 2. Dependence of the enthalpy change on mixing (corrected for dilution effects) an aqueous solution of κ-carrageenan ($C_p = 10^{-3}$ M) with aqueous CsCl (expressed as ionic strength, I) at different temperatures. Lozenges: T = 283.15 K; squares, T = 298.15 K; crosses, T = 308.15 K. Lines represent the theoretical fitting.

In conclusion, it has been shown that a full thermodynamic description of the interactions between metal ions and the IPS KC can be achieved using a simple, self-consistent extension of the CC theory of linear polyelectrolytes, even in the apparently difficult-to-tackle case of the gel state.

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