

## Supplementary Material

### 1. Intermediate values of $\Delta\bar{H}_{tr}^{excess}(\alpha)$ at the intermediate values of $\alpha$ , from $\alpha_1$ to $\alpha=1.0$ .

Values of  $\Delta\bar{H}_{tr}^{excess}$  (and incremental values) at intermediate values of  $\alpha$ , from the corresponding integral curves of panels (a) of Figures 2 (“salt”) and 3 (“water”) of the main paper.

a. Galacturonan in “Water”. $C_p = 6.4 \times 10^{-3}$ , $T = 25^\circ\text{C}$ , $R_i = 0$							
Conformation	$\alpha$		$\delta \alpha$	$\Delta\bar{H}_{tr}^{excess}$	$\delta\Delta\bar{H}_{tr}^{excess}$	$\Delta\bar{S}_{tr}^{excess}$	$\delta\Delta\bar{S}_{tr}^{excess}$
				Cal r.u. <sup>-1</sup>		cal r.u. <sup>-1</sup> K <sup>-1</sup>	
3 <sub>1</sub>	$\alpha_1$	0.13 <sub>2</sub>		0		0.00	
			0.10 <sub>8</sub>		2 <sub>4</sub>		0.0 <sub>7</sub>
	$\alpha_2$	0.24 <sub>0</sub>		2 <sub>4</sub>		0.0 <sub>7</sub>	
Conformational transition			0.36 <sub>0</sub>		51 <sub>0</sub>		1.5 <sub>3</sub>
2 <sub>1</sub>	$\alpha_3$	0.60 <sub>0</sub>		53 <sub>4</sub>		1.6 <sub>0</sub>	
			0.39 <sub>6</sub>		2 <sub>9</sub>		0.0 <sub>3</sub>
	$\alpha = 1$	0.99 <sub>6</sub>		56 <sub>3</sub>		1.6 <sub>3</sub>	

b. Galacturonan in “Salt”. $C_p = 5.0 \times 10^{-3}$ , $T = 25^\circ\text{C}$ , $R_i = 10$							
Conformation	$\alpha$		$\delta \alpha$	$\Delta\bar{H}_{tr}^{excess}$	$\delta\Delta\bar{H}_{tr}^{excess}$	$\Delta\bar{S}_{tr}^{excess}$	$\delta\Delta\bar{S}_{tr}^{excess}$
				cal r.u. <sup>-1</sup>		cal r.u. <sup>-1</sup> K <sup>-1</sup>	
3 <sub>1</sub>	$\alpha_1$	0.16 <sub>8</sub>		0		0.00	
			0.17 <sub>2</sub>		3 <sub>6</sub>		0.1 <sub>1</sub>
	$\alpha_2$	0.34 <sub>0</sub>		3 <sub>6</sub>		0.1 <sub>1</sub>	
Conformational transition			0.36 <sub>0</sub>		65 <sub>3</sub>		2.0 <sub>3</sub>
2 <sub>1</sub>	$\alpha_3$	0.70 <sub>0</sub>		69 <sub>0</sub>		2.1 <sub>4</sub>	
			0.30 <sub>0</sub>		3 <sub>7</sub>		0.1 <sub>3</sub>
	$\alpha = 1$	1.00 <sub>0</sub>		72 <sub>7</sub>		2.2 <sub>8</sub>	

### 2. Calculation of the “loosen.” contribution in the conformational transition interval.

To evaluate the *loosen.* contribution in the transition interval  $\alpha_2 \rightarrow \alpha_3$  two methods have been devised.

In Method I the value of  $(\Delta\bar{X}_{loosen.}^{excess})$  in the interval  $(\alpha_3 - \alpha_2)$  has been calculated as:

$$(\Delta\bar{X}_{loosen.}^{excess})_{(\alpha_3 - \alpha_2)} = \frac{(\Delta\bar{X}_{loosen.}^{excess})_{(\alpha_2 - \alpha_1)} + (\Delta\bar{X}_{loosen.}^{excess})_{(\alpha=1 - \alpha_3)}}{(\alpha_2 - \alpha_1) + (\alpha=1 - \alpha_3)} \cdot (\alpha_3 - \alpha_2).$$

In Method II the value of  $(\Delta\bar{X}_{loosen.}^{excess})$  in the interval  $(\alpha_3 - \alpha_2)$  has been calculated as:

$$(\Delta\bar{X}_{loosen.}^{excess})_{(\alpha_3 - \alpha_2)} = \left( \frac{(\Delta\bar{X}_{loosen.}^{excess})_{(\alpha_2 - \alpha_1)} / (\alpha_2 - \alpha_1) + (\Delta\bar{X}_{loosen.}^{excess})_{(\alpha=1 - \alpha_3)} / (\alpha=1 - \alpha_3)}{2} \right) \cdot (\alpha_3 - \alpha_2).$$

The results have been reported in the following Table, along with averages, and derived quantities.

	Galacturonan in “water”					Galacturonan in “salt”					
interval	$\delta \alpha$	$(\Delta\bar{H}_{loosen.}^{excess})^*$		$(\Delta\bar{S}_{loosen.}^{excess})^\dagger$		$\delta \alpha$	$(\Delta\bar{H}_{loosen.}^{excess})^*$		$(\Delta\bar{S}_{loosen.}^{excess})^\dagger$		
$(\alpha_2 - \alpha_1)$	$0.10_8$	2 <sub>4</sub>	2 <sub>4</sub>	0.0 <sub>7</sub>	0.0 <sub>7</sub>	$0.17_2$	3 <sub>6</sub>	3 <sub>6</sub>	0.1 <sub>1</sub>	0.1 <sub>1</sub>	
$(\alpha_3 - \alpha_2)$	$0.36_0$	<u>3</u> <sub>8</sub> <sup>a</sup>	<u>5</u> <sub>3</sub> <sup>b</sup>	<u>0.0</u> <sub>7</sub> <sup>a</sup>	<u>0.1</u> <sub>3</sub> <sup>b</sup>	$0.36_0$	<u>5</u> <sub>6</sub> <sup>a</sup>	<u>6</u> <sub>0</sub> <sup>b</sup>	<u>0.1</u> <sub>9</sub> <sup>a</sup>	<u>0.2</u> <sub>0</sub> <sup>b</sup>	
$(\alpha = 1 - \alpha_3)$	$0.39_6$	2 <sub>9</sub>	2 <sub>9</sub>	0.0 <sub>3</sub>	0.0 <sub>3</sub>	$0.30_0$	3 <sub>7</sub>	3 <sub>7</sub>	0.1 <sub>3</sub>	0.1 <sub>3</sub>	
	$(\Delta\bar{X}_{loosen.}^{excess})$	9 <sub>1</sub>	10 <sub>6</sub>	0.1 <sub>6</sub>	0.2 <sub>2</sub>	$(\Delta\bar{X}_{loosen.}^{excess})$	13 <sub>0</sub>	13 <sub>4</sub>	0.4 <sub>3</sub>	0.4 <sub>4</sub>	
	avg $\pm$ std	9 <sub>8</sub> $\pm$ 1 <sub>1</sub>		0.1 <sub>9</sub> $\pm$ 0.0 <sub>4</sub>		avg $\pm$ std	13 <sub>2</sub> $\pm$ 3		0.4 <sub>4</sub> $\pm$ 0.0 <sub>1</sub>		
	$\Delta\bar{X}_{3_1 \rightarrow 2_1}^{excess}$	47 <sub>2</sub>	45 <sub>7</sub>	1.4 <sub>6</sub>	1.4 <sub>0</sub>	$\Delta\bar{X}_{3_1 \rightarrow 2_1}^{excess}$	59 <sub>7</sub>	59 <sub>3</sub>	1.8 <sub>4</sub>	1.8 <sub>3</sub>	
	avg $\pm$ std	46 <sub>5</sub> $\pm$ 1 <sub>1</sub>		1.4 <sub>3</sub> $\pm$ 0.0 <sub>4</sub>		avg $\pm$ std	59 <sub>5</sub> $\pm$ 3		1.8 <sub>4</sub> $\pm$ 0.0 <sub>1</sub>		
	recalculated	$\Delta\bar{X}_{tr}^{excess}$	56 <sub>3</sub> $\pm$ 1 <sub>5</sub>		1.6 <sub>3</sub> $\pm$ 0.0 <sub>6</sub>		$\Delta\bar{X}_{tr}^{excess}$	72 <sub>7</sub> $\pm$ 4		2.2 <sub>8</sub> $\pm$ 0.0 <sub>1</sub>	

“water” Salt-free aqueous solution,  $C_p = 6.4 \times 10^{-3}$ ,  $T = 25^\circ\text{C}$ ,  $R_i = 0$ ;

“salt” In aqueous 0.05 M NaClO<sub>4</sub>,  $C_p = 5.0 \times 10^{-3}$ ,  $T = 25^\circ\text{C}$ ,  $R_i = 10$ .

\* Units of enthalpy changes in cal mole r.u.<sup>-1</sup>.

† Units of entropy changes in cal mole r.u.<sup>-1</sup> K<sup>-1</sup>.

<sup>a</sup> Method I.

<sup>b</sup> Method II.

$\bar{X}$  =  $\bar{H}$ ,  $\bar{S}$ .

### 3. More on the Thermodynamics of Association.

3.1. The values of  $\Delta\bar{S}_{exper.}^{DSC, T_m}$  as a function of  $C_p$  can be easily calculated from equations 2 and 4 of the main paper:

$$\Delta\bar{S}_{exper.}^{DSC, T_m}(C_p) = \frac{\Delta\bar{H}_{exper.}^{DSC}(C_p)}{T_m(C_p)} = \frac{(\Delta\bar{H}_{exper.}^{DSC})_{C_p=0} + \frac{d\Delta\bar{H}_{exper.}^{DSC}}{dC_p} \cdot C_p}{(T_m)_{C_p=0} + \frac{dT_m}{dC_p} \cdot C_p} \quad S1$$

It can be easily demonstrated that equation S1, for  $C_p \rightarrow 0$ , becomes:

$$\lim_{C_p \rightarrow 0} \Delta\bar{S}_{exper.}^{DSC, T_m}(C_p) = (\Delta\bar{S}_{tr}^{DSC, T_m})_{C_p=0} + \left( \frac{1}{(T_m)_{C_p=0}} \right) \cdot \left( \frac{d\Delta\bar{H}_{exper.}^{DSC}}{dC_p} - (\Delta\bar{S}_{exper.}^{DSC})_{C_p=0} \cdot \frac{dT_m}{dC_p} \right) \cdot C_p \quad S2$$

and then:

$$\lim_{C_p \rightarrow 0} \Delta\bar{S}_{exper.}^{DSC, T_m}(C_p) = (\Delta\bar{S}_{tr}^{DSC, T_m})_{C_p=0} + \frac{d\Delta\bar{S}_{exper.}^{DSC, T_m}}{dC_p} \cdot C_p \quad S3$$

As in equation 3 of the main paper, it holds:

$$\frac{d\bar{\Delta S}_{exper.}^{DSC,T_m}}{dC_p} \equiv \frac{d\Delta S_{separ.}^{DSC,T_m}}{dC_p} = - \frac{d\Delta S_{assoc.}^{DSC,T_m}}{dC_p} \quad S4$$

The plot of  $\bar{\Delta S}_{exper.}^{DSC,T_m}(C_p)$  is linear ( $R^2 = 0.9999$ ) with intercept  $(\bar{\Delta S}_{tr}^{DSC,T_m})_{C_p=0} = +2.87 \text{ cal mole r.u.}^{-1} \text{ K}^{-1}$  (as per equation 5 of the main paper) and slope  $-0.07085 \text{ cal mole r.u.}^{-1} \text{ K}^{-1} (\text{wt}\%)^{-1}$ , confirming the result obtained from equation 5.

3.2. Both  $\Delta H_{assoc.}^{DSC}$  and  $\Delta S_{assoc.}^{DSC,T_m}$  are extensive properties, for which it holds:

$$\Delta H_{separ.}^{DSC} = f_{assoc.}(C_p) \cdot (\bar{\Delta H}_{separ.}^{DSC})^{micro.} \text{ and } \Delta S_{separ.}^{DSC,T_m} = f_{assoc.}(C_p) \cdot (\bar{\Delta S}_{separ.}^{DSC,T_m})^{micro.} \quad S5$$

being  $(\bar{\Delta H}_{assoc.}^{DSC})^{micro.}$  and  $(\bar{\Delta S}_{assoc.}^{DSC,T_m})^{micro.}$  the “intrinsic” values of the enthalpy and of the entropy change of association, respectively; they are *microscopic (micro.)* thermodynamic functions, referring to the polymer repeating unit. Finally:

$$\bar{\Delta H}_{exper.}^{DSC}(C_p) = (\bar{\Delta H}_{exper.}^{DSC})_{C_p=0} + (\bar{\Delta H}_{separ.}^{DSC})^{micro.} \cdot \frac{d f_{assoc.}(C_p)}{dC_p} \cdot C_p \quad S6$$

and:

$$\bar{\Delta S}_{exper.}^{DSC,T_m}(C_p) = (\bar{\Delta S}_{tr}^{DSC,T_m})_{C_p=0} + (\bar{\Delta S}_{separ.}^{DSC,T_m})^{micro.} \cdot \frac{d f_{assoc.}(C_p)}{dC_p} \cdot C_p \quad S7$$

The ratio  $(\bar{\Delta H}_{separ.}^{DSC})^{micro.} / (\bar{\Delta S}_{separ.}^{DSC,T_m})^{micro.} = \underline{230.3 \text{ K}}$  is the characteristic temperature,  $(T_m)_{separ.}$ , of the separation/association process.

3.3. It can be easily demonstrated that, in any association process, for  $C_p \rightarrow 0$  the fraction of associated material is linearly proportional to  $C_p$ , i.e.  $\frac{d f_{assoc.}(C_p)}{dC_p} = \text{const.}$  In fact, if M is the molar concentration of non-associated LMP macromolecules and D the molar concentration of associated LMP macromolecules, being  $C_0$  the initial molar concentration of non-associated LMP macromolecules (with  $C_0 = (C_p) / n$ , with n the number of repeating units per chain) and  $f_{assoc.}$  the fraction of associated material, it is possible to write:

$$K = D / M^2 = D / (C_0 - D)^2 \quad S8$$

For  $C_0 \rightarrow 0$ ,  $D \ll C_0$  and then  $(C_0 - D) \approx C_0$ ; it follows that:

$$K = (1/2 \cdot C_0 \cdot f_{assoc.}) / (C_0)^2 \quad S9$$

and

$$f_{assoc.} = (2 / n) \cdot K \cdot C_p = 2 \cdot K_{assoc.} \cdot C_p \quad S10$$

It holds:

$$K_{assoc.} = e^{\left( -(\Delta \bar{G}_{assoc.}^{DSC})^{micro.} / R \cdot T \right)} = e^{\left( (\Delta \bar{G}_{separ.}^{DSC})^{micro.} / R \cdot T \right)} \quad S11$$

Being  $K_{assoc.}$  a constant by definition, both  $(\Delta \bar{H}_{separ.}^{DSC})^{micro.}$  and  $(\Delta \bar{S}_{separ.}^{DSC, T_m})^{micro.}$  are constant. Moreover, since  $\frac{d f_{assoc.}(C_p)}{d C_p} = 2 K_{assoc.}$  is always positive, due to the positive  $C_p$ -dependence of any intermolecular association process, and given the negative values of both  $\frac{d \Delta H_{separ.}^{DSC}}{d C_p}$  and of  $\frac{d \Delta S_{separ.}^{DSC, T_m}}{d C_p}$ , it implies that the separation process is intrinsically exothermic and exergonic, as expected for the breakdown of hydrophobic interactions.

3.4. For the separate evaluation of the  $\Delta H_{3_1 \rightarrow 2_1}^{DSC}$  and  $\Delta \bar{H}_{loosen.}^{DSC}$  contributions to the thermal transition, this procedure was followed for each pH value from 1.6 to 4.0:

a. Starting from  $(\Delta \bar{H}_{exper.}^{DSC})_{C_p=3\%} = (\Delta H_{separ.}^{DSC})_{C_p=3\%} + \Delta H_{3_1 \rightarrow 2_1}^{DSC} + \Delta \bar{H}_{loosen.}^{DSC}$ , the sum  $\Delta \bar{H}_{tr}^{DSC} = \Delta H_{3_1 \rightarrow 2_1}^{DSC} + \Delta \bar{H}_{loosen.}^{DSC}$  was calculated as  $(\Delta \bar{H}_{exper.}^{DSC}(C_p) - \Delta H_{separ.}^{DSC}(C_p))$  (data from Figure 12a of the main paper).

b. For all cases  $pH \leq 3.0$ , it was assumed that the system at 10 °C was completely in the  $3_1$  helical form (see Figure 13a of the main paper):  $(f_{3_1})_{T=10\text{ }^\circ\text{C}} = 1$ .

c. The maximum value of  $\Delta H_{3_1 \rightarrow 2_1}^{DSC}$  was set equal to  $\Delta \bar{H}_{3_1 \rightarrow 2_1}^{excess} = 0.59 \text{ kcal mol}^{-1}$  (see Table 2). For all cases (namely  $2.0 \leq pH \leq 3.0$ ) in which  $\Delta \bar{H}_{tr}^{DSC} \geq \Delta \bar{H}_{3_1 \rightarrow 2_1}^{excess}$ ,  $\Delta H_{3_1 \rightarrow 2_1}^{DSC}$  was set equal to  $\Delta \bar{H}_{3_1 \rightarrow 2_1}^{excess}$ . This corresponds to 100%  $3_1 \rightarrow 2_1$  transformation for the thermal transition  $10\text{ }^\circ\text{C} \rightarrow 85\text{ }^\circ\text{C}$ .

d. For the range  $2.0 \leq pH \leq 3.0$ ,  $\Delta \bar{H}_{loosen.}^{DSC}$  was calculated from  $\Delta \bar{H}_{loosen.}^{DSC} = \Delta \bar{H}_{tr}^{DSC} - \Delta H_{3_1 \rightarrow 2_1}^{DSC}$ . The values of  $\Delta \bar{H}_{loosen.}^{DSC}(pH)$  steadily decrease upon decreasing pH (see Figure 12a of the main paper), perfectly paralleling the decrease of both molar ellipticity and optical activity with decreasing pH (see Figure 7 of the main paper). Extrapolation of the  $\Delta \bar{H}_{loosen.}^{DSC}(pH)$  curve to pH values below 2.0 shows that, at  $pH = 1.6$ ,  $\Delta \bar{H}_{loosen.}^{DSC} = 0$ .

e. At  $pH = 1.6$ , being  $\Delta \bar{H}_{tr}^{DSC} < \Delta \bar{H}_{3_1 \rightarrow 2_1}^{excess}$ , it was set:  $\Delta \bar{H}_{tr}^{DSC} = (f_{3_1})_{T=85\text{ }^\circ\text{C}} \Delta \bar{H}_{3_1 \rightarrow 2_1}^{excess}$ , namely only a fraction of the  $3_1$  helix was supposed to transform to the  $2_1$  one upon heating (see Figure 12b of the main paper).

f. For the two cases of pH = 3.5 and pH = 4.0, also according to Ravanat's results (see Figure 13a of the main paper), it was assumed that  $(f_{31})_{T=10\text{ }^{\circ}\text{C}} < 1$ .

g. In the absence of additional information, it was assumed that the reduction of the  $3_1 \rightarrow 2_1$  term and of the "loosening" one were equally proportional to the reduction of  $\Delta \bar{H}_{tr}^{DSC}$  with respect

to its maximum value at pH = 3.0, namely:  $(f_{31})_{pH=3.5 \text{ or } 4.0}^{T=10\text{ }^{\circ}\text{C}} = \frac{(\Delta \bar{H}_{tr}^{DSC})_{pH=3.5 \text{ or } 4.0}}{(\Delta \bar{H}_{tr}^{DSC})_{pH=3.0}}$ .

Hence,  $(\Delta \bar{H}_{3_1 \rightarrow 2_1}^{DSC})_{pH=3.5 \text{ or } 4.0} = (f_{31})_{pH=3.5 \text{ or } 4.0}^{T=10\text{ }^{\circ}\text{C}} (\Delta \bar{H}_{3_1 \rightarrow 2_1}^{excess})_{pH=3.0}$ , and  $(\Delta \bar{H}_{loosen.}^{DSC})_{pH=3.5 \text{ or } 4.0} = (f_{31})_{pH=3.5 \text{ or } 4.0}^{T=10\text{ }^{\circ}\text{C}} (\Delta \bar{H}_{loosen.}^{excess})_{pH=3.0}$ .

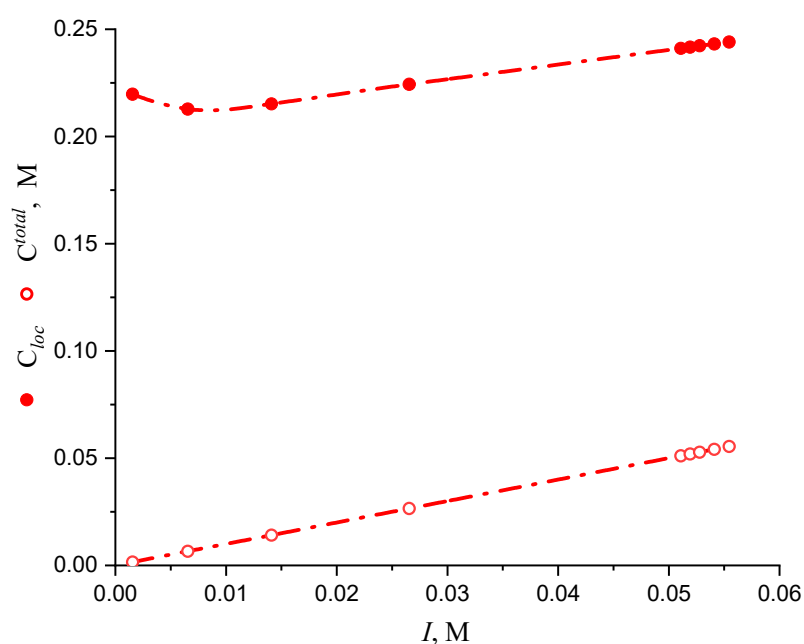
#### 4. On the possible sources of deviation from theory of the enthalpy of mixing data.

4.1. A possible first explanation of the observed endothermic heat of mixing is that the interaction of the monovalent sodium ion with the pectate polyanion is accompanied by an endothermic heat effect similar to those shown by the divalent counterion  $Mg^{2+}$  [76,101] and, much more so, by  $Ca^{2+}$  [25], i.e. stemming from a specific affinity interaction ( $\Delta \bar{H}^{aff} > 0$ ). However, to produce a measurable endothermic contribution  $((\Delta \bar{H}^{mix})_{EXCESS})$  any intensive value of  $\Delta \bar{H}^{aff}$  is to be multiplied by the change in the fraction of condensed counterions accompanying the specific interaction,  $\Delta r$ :  $\Delta \bar{H}^{excess} = \Delta \bar{H}^{aff} \Delta r$ ,  $C_p$ ,  $C_p$  being the equivalent polymer concentration. G.S. Manning, in one of his fundamental works on the elaboration of the CC theory, highlighted the "*extraordinary stability of the charge fraction*" [110], and consequently of the fraction of condensed counterions,  $r$ , over a wide range of ionic strength change. This theoretical result (which was corroborated by strong experimental evidence) is strongly supported by the pioneering finding of Rinaudo and Ravanat for poly(galacturonic acid) that "*The osmotic coefficients for sodium ( $\phi_{Na}$ ) (Fig. 3) are in agreement with the values predicted by the theories of Manning ( $\phi_M$ ) and Katchalsky ( $\phi_K$ ) and introducing in the theoretical expressions for  $\phi$ , the  $\lambda_{app}^{Na}$  value obtained from pH measurements.*" [7].

Altogether, those two experimental observations rule out the possibility that the fraction of the condensed  $Na^+$  counterions change upon changing the ionic strength of the medium,  $I$ , namely point to a constant value of  $r$ , and to  $\Delta \bar{H}^{excess} = 0$  being  $\Delta r = 0$ .

4.2. Next, the (remote) possibility was considered that the effective local concentration of condensed  $Na^+$  ions (at constant fraction,  $r$ ) undergoes a major change because of a change of the condensation volume, so to realize a strong non-ideal behavior. For example, in the case of DNA,

the local concentration of monovalent counterions is about 1.2 M, which makes any difference with the external ionic concentration (typically in the order of  $10^{-2}$  M to  $10^{-1}$  M) very large. Using the definition of the local concentration,  $C_{loc} = r / \bar{V}_p$  [103], and that of  $\bar{V}_p$ , the molar volume of condensation (in L eq<sup>-1</sup>), and the proper values of the variables, the values of  $C_{loc}$  have been calculated for Na<sup>+</sup> pectate for a range of  $I$  values from 0 to 0.06 M. The results have been reported in Figure S1.



**Figure S1.** Dependence on the total ionic strength,  $I$ , of the local concentration of condensed Na<sup>+</sup> counterions (full red circles) and of the total concentration of Na<sup>+</sup> counterions (open red circles). Concentration of sodium pectate:  $3.5 \times 10^{-3}$  eq L<sup>-1</sup>.

It is clearly evident that the values of  $C_{loc}$  are in the order of  $10^{-1}$  M, namely much smaller than that of DNA clearly because of the much smaller charge density, but, more important, the maximum variation,  $\delta C_{loc}$ , is about 0.02 M. An estimate of the possible effects can be done considering that *i*) the difference in the relative apparent molal enthalpy of NaClO<sub>4</sub> in “water” at 25 °C from 0.2278 m to 0.2050 m ( $\delta m = 0.0228$  m) is +2 cal mol<sup>-1</sup> [104] and *ii*) the experimental heat of dilution of NaCl at 25 °C from 0.2996 m to 0.1492 m ( $\delta m = 0.1504$  m) is  $+3.6 \pm 0.7$  cal mol<sup>-1</sup> [105].

It is clearly evident that even the largest variation of  $C_{loc}$  would imply an endothermic effect which is at least one full order of magnitude smaller than that experimentally observed for mixing sodium pectate with sodium perchlorate.

## 5. More on Hofmeister and Lyotropic Effects in Polysaccharide Systems.

5.1 As to perchlorate/polysaccharide systems, literature papers are essentially focused on practical applications [106,107].

5.2 Specific effects have been reported as to the interactions of ionic polysaccharides with both cations and anions, up to severely affecting their conformational equilibria:

- *Poly-L-gulonate chain segments show substantial enhancement (–50%) of c.d. ellipticity in the presence of excess of  $K^+$ , with smaller changes for other univalent cations:  $Li^+ < Na^+ < K^+ > Rb^+ > Cs^+ > NH_4^+$ . The maximum c.d. change is attained by 0.3 M with no further increase at higher concentrations of cation. No significant dependence on polymer concentration is observed [108].*

- *From the conformational change at constant ionic concentration in the cooling curves, we observed the same sequence as described by Payens and Snoeren<sup>16</sup> for the gelling temperature:  $Rb^+ > Cs^+ > K^+ > NH_4^+ > N(CH_3)_4^+ > Na^+ > Li^+$  [109].*

- *Anions differ in their capacity to stabilize the furcellaran helix in the sequence  $Cl^- < NO_3^- < Br^- < SCN^- < I^-$ . The iodide and thiocyanate anions impede aggregation and gel formation [110].*

- *Anions stabilize the helical conformer of both carrageenans according to the sequence  $Cl^- < NO_3^- < Br^- < SCN^- < I^-$  [111].*

5.3 Specific interactions can modulate the gelation behavior of polysaccharides:

- *Even in the absence of alkali, the salting-out sodium sulfate was found to be capable of making KGM form a thermally irreversible gel at neutral conditions upon heating...*

*Upon addition of sodium sulfate the behavior of KGM in water changed from a viscoelastic fluid at room temperature to an increasing stiff gel at elevated temperatures....*

*ESR measurements showed that the addition of sodium sulfate into either water or KGM aqueous solution led to a significant increase in rotational correlation time of the radical, consistent with the increase in viscosity and moduli in rheological experiments [112].*

- *Enthalpy estimations from a combined thermodynamic and optical study of the agarose sol-gel conversion reveal that both the coil-helix transition and helix-helix interactions reduce with the addition of sodium sulfate. Examination of the hydration characteristics shows that the addition of sodium sulfate in the aqueous agarose solutions weakens the gel structure by weakening the agarose-water interactions and facilitates the easy release of water from gel network. The decrease of water mediating the agarose helices upon gelation with the increase of sodium sulfate concentration in the aqueous agarose solutions is also confirmed from pyrene fluorescence spectra. Analysis of water structure from FTIR measurements shows*

*the strengthening of hydrogen bonding of water molecules in the gel which tends to weaken with the subsequent addition of sodium sulfate [113].*

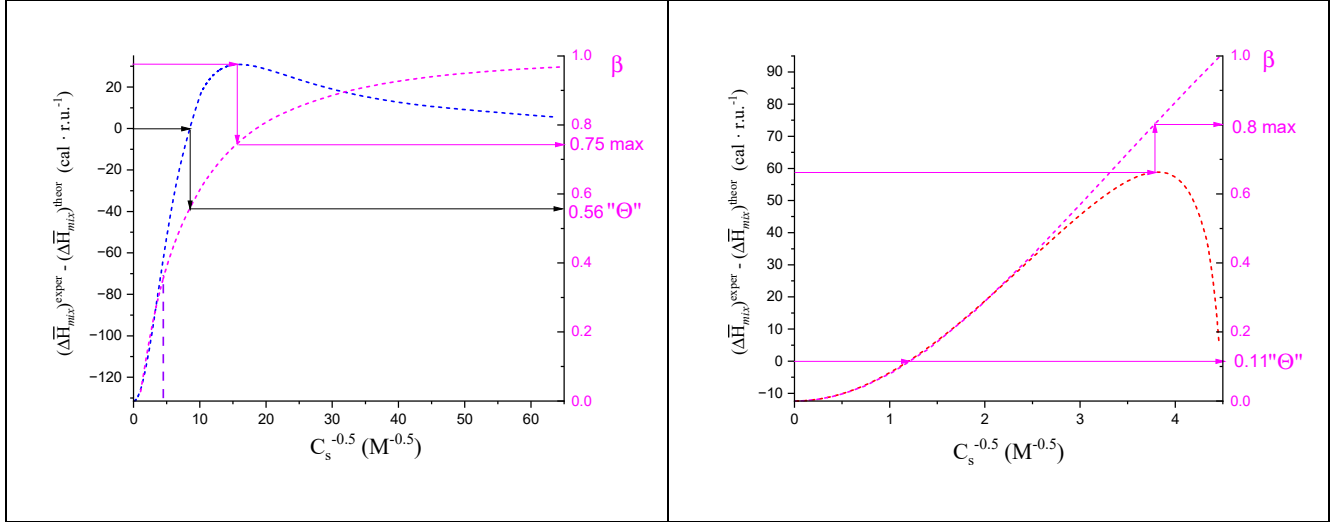
## 6. On the Coupling of the Polyelectrolyte Aspects with the Lyotropic Ones.

Figure S2 is the re-plotting of the two curves of Figure 17 of the main paper as a function of the inverse of the square-root of the low MW salt concentration,  $C_s^{-0.5}$ , for the “water” case (panel (a)), and for the “salt” case (panel (b)). This variable is usually taken as the independent one in analyzing polyelectrolyte behavior [94]. On the r.h.s. the newly defined variable  $\beta$  has been plotted also versus  $C_s^{-0.5}$ .  $\beta$ , which can be looked upon as the “degree of un-screening”, has been defined in the main text.

Interestingly, the values of  $\beta$  at the maximum of  $(\Delta\bar{H})_{mix}^{excess}$  are rather close in the two cases, namely 0.75 for the former case and 0.80 for the latter one, suggesting that the maximum loosening effect of an increase of  $\text{ClO}_4^-$  concentration at  $\alpha = 1.0$  - after charging from  $\alpha = \alpha_1$  to  $\alpha = 1.0$  - is essentially controlled by the physical interactions of polyelectrolyte nature. On the opposite, the values of  $\beta$  at which the balance between the polyelectrolyte interactions and the lyotropic ones equalize (namely at which  $(\Delta\bar{H})_{mix}^{excess} = 0.0$ :  $\beta_\Theta$ ) are very different for the two systems:  $\beta_\Theta$  is as high as 0.59 for “water” and as low as 0.11 for “salt”. Those values correspond to  $[\text{NaClO}_4] = 0.015 \text{ M}$  and  $0.67 \text{ M}$  and to the values of the Debye length,  $\kappa^{-1}$ , of  $23.6 \text{ \AA}$  and  $3.7 \text{ \AA}$ , respectively (incidentally, the value of  $\kappa^{-1} = 4.35 \text{ \AA}$  - that is equal to the average distance of uronate charges at  $\alpha = 1.0$  [8] - corresponds to  $[\text{NaClO}_4] = 0.49 \text{ M}$ ). The subscript “ $\Theta$ ” has been used to highlight the condition of equality of the opposing interactions, a (kind of)  $\Theta$ -condition of the polyelectrolyte. The much lower value for galacturonan in  $0.05 \text{ M NaClO}_4$  is a measure of the ability of the chaotropic anion, in due concentration, to withstand the “re-tightening” effect of the progressively shielded polymer negative charges.

(a)	(b)
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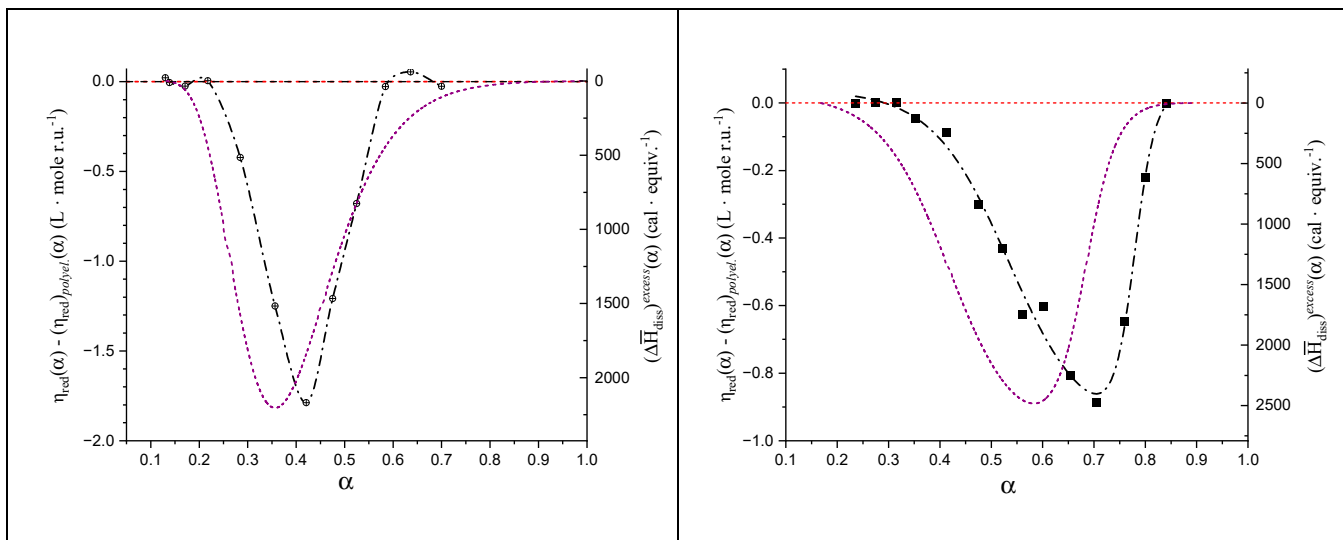


**Figure S2.** Dependence on the inverse of the square-root of the molar concentration of  $\text{NaClO}_4$  of (i) the difference between the experimentally determined heat of mixing (l.h.s. scale) for galacturonan in water (panel (a), blue dashed curve) and in 0.05 M  $\text{NaClO}_4$  (panel (b) red dashed curve) and the theoretical value calculated on the basis of the Counterion Condensation theory (magenta dashed curve),  $(\Delta\bar{H})_{mix}^{excess}$ , and (ii) the fraction of unscreened charge,  $\beta$  (r.h.s. scale). "max" and "Θ" stand for the value of  $\beta$  corresponding to value at maximum of the difference enthalpic curve and at  $(\Delta\bar{H})_{mix}^{excess} = 0$ , respectively. The vertical purple dashed segment in panel (a) corresponds to the maximum value of the abscissa of panel (b).

## 7. On the Viscometric behavior of Galacturonan as Compared to that of a "Normal" Weak Polyacid.

Figure S3 reports the dependence of the difference between the experimental values of the reduced viscosity of galacturonan as a function of  $\alpha$  and the dashed-dotted baseline from Figure 19 of the main paper for both the "water" and the "salt" cases. The corresponding difference curves between the experimental  $\Delta\bar{S}_{diss}(\alpha)$  and the baseline (from Figures 2a and 3a of the main paper) have also been reported. In both cases the maximum of the viscometric curves lags behind the corresponding enthalpic maximum, indicating that the development of the whole-chain rheological behavior is uncoupled from the change in internal energy. Cooperative effects on the former scale require that the latter changes be largely attained to allow establishing changes at the mesoscopic scale. At variance, using the initial viscometric behavior of the  $3_1$  rigid conformation as the reference reconciles the rheological and the enthalpic behavior as shown 20 (b) and thereafter discussed.

(a)	(b)
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**Figure S3.** Dependence on  $\alpha$  of (i) the difference between the experimental reduced viscosity and the baseline expected for a “normal” weak polyacid (dashed-dotted curves of Figure 19 of the main paper) (black symbols and dash-dotted curves) and (ii) the excess enthalpy of dissociation (from panels (a) of Figures 2 and 3 of the main paper) (purple dashed curves). (a) galacturonan at 25 °C in “water”, (b) galacturonan at 25 °C in “salt”.