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Preliminary communication

Monomer composition and acetyl content as main determinants of the ionization behavior of alginates

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As a part of our investigations on the physicochemical properties of natural carboxylated polysaccharides in dilute aqueous solution[1,2], we have studied the ionization behavior of two different alginate samples (*A* and *B*: see Table I). Motivation for this study derives from the marked influence that sugar composition and sequence may have on the solution and gelation properties of ionic polysaccharides[3,4]. Although *A* and *B* do not represent extreme examples in the range of chemical composition of the alginates (*i.e.*, mannuronic/guluronic ratio and degree of acetylation), clear differences are detectable in their polyelectrolytic behavior. This adds interest to a thermodynamic investigation of different alginates in aqueous solution to help unravel the correlation between structure and solution behavior.

The calorimetric enthalpy of dissociation data shown in Fig. 1 indicate that the ionization processes of alginates *A* and *B* are energetically different at both low *and* high degrees of ionization (α). Overall, the ionized state of *A* is more favored by enthalpy than that of *B*.

TABLE I

CHEMICAL COMPOSITION AND DOUBLET FREQUENCIES OF ALGINATE SAMPLES[a]

	F_M	F_G	F_{MM}	F_{MG}	F_{GM}	F_{GG}	*Ac* (%)
Sample A[b]	0.55	0.45	0.40	0.15	0.15	0.30	0
Sample B[c]	0.37	0.63	0.24	0.13	0.13	0.50	8

[a] The fractions of mannuronate (F_M) and guluronate (F_G) residues, the doublet frequencies (F_{MM}, F_{MG}, F_{GG}), and the percentage of acetylation were determined by p.m.r. spectroscopy. [b] Algal alginate, commercial sample (Fluka). [c] Bacterial alginate from *Azotobacter vinelandii* lot S-35 (gift from Dr. K. C. Symes, Tate & Lyle, Ltd., U.K.).

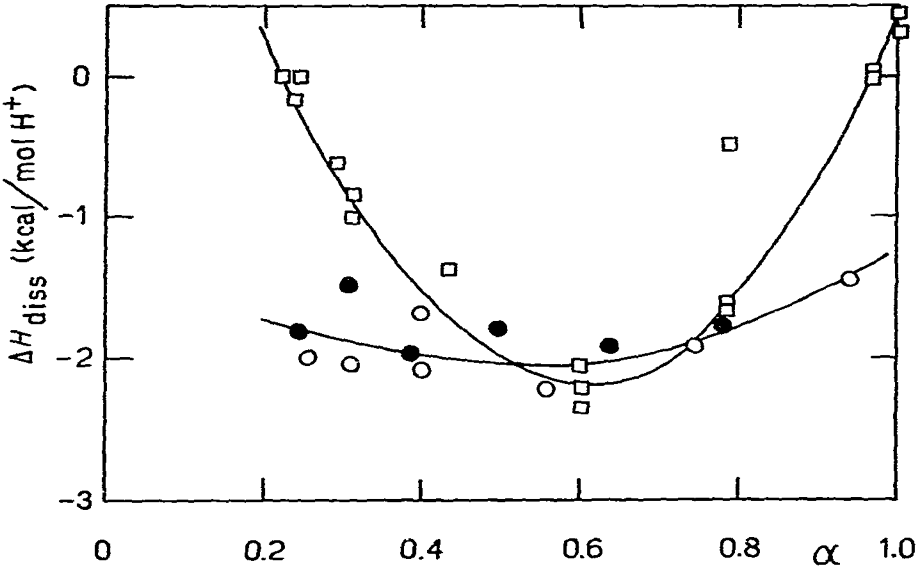

Fig. 1. Enthalpy changes on proton dissociation (ΔH_{diss}) of alginic acids *A* (○, ●) and *B* (□) (from ref. 1) as a function of the degree of ionization (α) in water at 25°; polymer concentration, 10^{-3} equiv./litre. For each α value, the observed heat of reaction of the polysaccharide with aqueous HCl, corrected for the heats of dilution of polymer and acid, has been normalized by the actual moles of protons involved in the protonation, as derived from potentiometric titration data. LKB 10700-2 batch-type (□, ○) and flow-type (●) isothermal microcalorimeters were used^2.

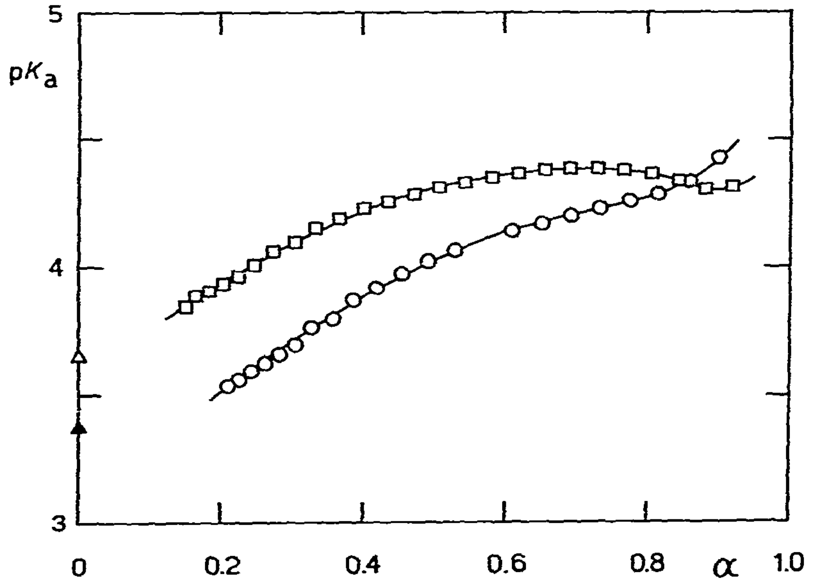

Fig. 2. Apparent p*K*a dependence on α for alginic acids *A* (○) and *B* (□) titrated with NaOH in water at 25°; polymer concentration, 5.2 × 10^{-3} equiv./litre. Values of p$K°$ for L-guluronic (△) and D-mannuronic acid (▲) are also reported from ref. 5.

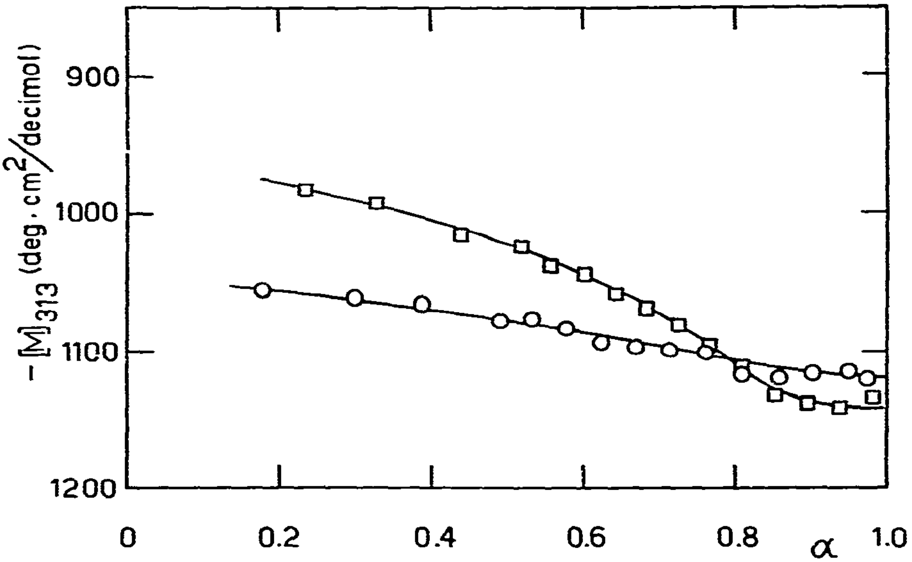

Fig. 3. Dependence on the degree of ionization (α) of the molar optical rotation ($[M]_{313}$) of alginic acids *A* (○) and *B* (□) in water at 25°. A Perkin–Elmer 141 M polarimeter was used; the solution was titrated with M NaOH, and the α values were obtained by potentiometric titration under equal conditions.

These results find a counterpart in the potentiometric data (Fig. 2) which show that, at low α, alginate *A* is a slightly stronger acid than alginate *B*. The largest part of this effect can be ascribed to the fact that the former is richer in mannuronic acid residues[5].

Differences in the course of ionization of *A* and *B* are also indicated by optical activity data (Fig. 3). On increasing α, the molar rotation of *A* changes smoothly, whereas that of *B* exhibits a sigmoidal change.

Surprisingly, the volume change (dilatometric) measurements on proton addition to the salt form of alginate *A* not only gave a straight line over the whole interval of α ($0 < \alpha < 1$), but the slope of this line (*i.e.*, the differential volume of dissociation, $\Delta V_{diss} = -11.5$ mL/equiv.) was coincident with that already reported[1] for alginate *B*. The apparent insensitivity of the (incremental) solvation properties of ionic polysaccharides to different conformational situations in water has been reported for pectic acid ($\Delta V_{diss} = -13.4$ mL/equiv.), which undergoes a pH-induced conformational transition[2].

To investigate further the solution behavior of *A* and *B* at $\alpha \sim 1$, the heat of dilution (ΔH_{dil}) has been studied. The plot of ΔH_{dil} against the logarithm of the final polymer concentration in equiv./litre (Fig. 4) shows that the behavior of alginate *B* is anomalous, whereas that for *A* is very much like that found for other ionic polysaccharides[6,7]. However, deacetylation of *B* yielded a product which behaved similarly to *A*, at least as far as the enthalpy of dilution at $\alpha \sim 1$ is concerned (Fig. 4).

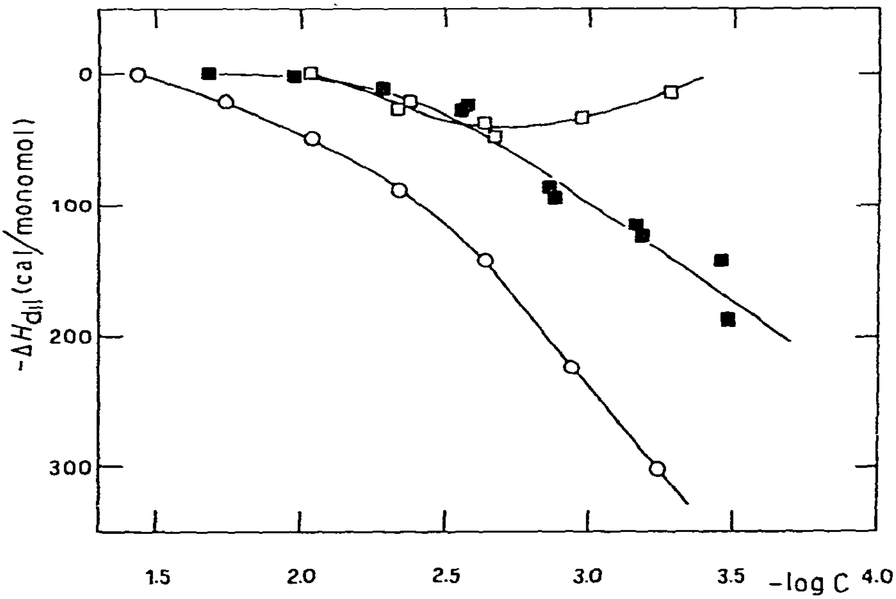

Fig. 4. Dependence on the –log of the final polymer concentration of the enthalpy of dilution (ΔH_{dil}) of alginates ($\alpha \sim 1$, Na^+ salt) *A* (○) and *B* (□) and of deacetylated *B* (■) in water at 25°. The zero in the ordinate is arbitrarily fixed at the highest concentration used for each different sample. Deacetylation of *B* was effected with ammonia (1 h at 60°).

Thus, significant differences in the polyelectrolytic behavior of alginates *A* and *B* have been discerned at low degrees of dissociation (heat of dissociation and potentiometric data) and also around full neutralization (optical activity and heat of dilution data). In the low α region, the different content of mannuronic and guluronic residues of *A* and *B* may govern the properties considered, but we believe that the acetyl content of *B* (~8%) may be mainly responsible for its somewhat anomalous properties at high α values. It is possible that even such a modest amount of substitution could produce significant conformational effects, because acetyl groups seriously perturb stereoregular sequences, as in partially acetylated poly(vinyl alcohol)[8] and carboxymethylated amylose[9]. This problem is being studied further.

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