Comment on "The Helix–Coil Transition of an Ionic Polysaccharide Probed by Counterion Self-Diffusion Measurements" by L. Piculell and R. Rymdén

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ι-Carrageenan undergoes a helix–coil transition in aqueous solution. There is disagreement on the association state of the helix, which could be a single-helical chain or a double helix. Piculell and Rymdén[1] argue for the double helix on the basis of a comparison of polyelectrolyte theory with their data for the sodium counterion self-diffusion coefficient in solutions containing only the polymer salt.

The theory used by these authors, based on the Poisson–Boltzmann equation in the context of the cell model, is not without problems. The cell model requires the polyions to be aligned, thus endowing the solution with at least some short-range quasi-crystalline properties. There is no evidence for short-range order in the authors' system nor perhaps is any expected at the low polymer concentrations used. The Poisson–Boltzmann equation fails to predict the sharp breaks at the counterion condensation point observed in counterion self-diffusion measurements.[2] Possibly symptomatic of these deficiencies is the authors' prediction of a counterion diffusion coefficient that varies with concentration, in contrast to their experimental observation of concentration invariance of this quantity.

Further, calculated diffusion coefficients are substantially higher than the observed values (particularly the "contact radius" values, which should be the more realistic of the two sets of theoretical values presented). The authors do not appear to have made a strong case for the double helix on the basis of this theory.

The polyelectrolyte limiting law for the counterion diffusion coefficient in solutions containing only the polymer salt provides a unique value for each conformation.[3] There is no dependence on polymer concentration. The authors observe no such dependence in the range studied. They may, therefore, be working in conditions of applicability of the limiting law. This formula, eq 49 of ref 3, predicts the value 0.61 for the diffusion ratio (sodium diffusion in the presence and absence of polyion) in solutions of the coil form of ι-carrageenan, while the authors measure a value 0.72. Thus, when the conformation is known, the limiting law prediction bears comparison with measurement. For a putative single helix, the prediction is 0.52, close to the measured value 0.56 for the helix form. For a double helix the prediction would be 0.27, much lower than the measured value 0.56. On this basis, the authors' data can be interpreted as suggesting the presence of a single-stranded helix.

References and Notes

(1) Piculell, L.; Rymdén, R. *Macromolecules* **1989**, *22*, 2376.
(2) Henningson, C. T.; Karluk, D.; Ander, P. *Macromolecules* **1987**, *20*, 1286.
(3) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 934.

Registry No. ι-Carrageenan, 9062-07-1.