New insights into the mechanism of gelation of alginate and pectin: Charge annihilation and reversal mechanism

Abstract

Studies have been undertaken on the binding of Mn2+ ions to two alginate samples of different mannuronate:guluronate ratios (M:G), a sample of low-ester amidated pectin and poly(acrylic acid) (PAA). The binding of Ca2+ ions has also been included for the latter for comparison. The binding curves showed an initial steep rise at low additions of Mn2+ or Ca2+ indicating that all of the ions were bound to the polymer chains with none remaining in solution. At higher additions, the binding curves showed a plateau region and the maximum amount bound, θ, was found to be 0.2, 0.2, 0.25, and 0.33 mol M2+/mol COO- for high M:G alginate, low M:G alginate, pectin, and PAA, respectively. The binding curves for Mn2+ and Ca2+ with PAA were superimposable. In all cases, θ was less than the stoichiometric equivalent and also less than predicted by Manning counterion condensation theory. The linear charge density, ξ, for the polymers is 1.49, 1.55, 1.62, and 2.85, and it was found that at maximum binding the effective linear charge density, ξeffective, decreased to a value close to 1 in each case and not 0.5 as predicted from Manning's two-variable theory. The mobility of the PAA chains has been followed by electron spin resonance spectroscopy using nitroxide spin labels covalently attached to the polymer, and the gelation of the pectin and alginate samples has been monitored using small deformation oscillatory experiments. For PAA at maximum binding, it was noted that there was a loss of chain mobility and precipitation. For pectin and alginate, gelation occurred and the stoichiometric ratio for maximum binding corresponded to the stoichiometric ratio for the maximum in G‘. Precipitation and gelation are attributed to the formation of polymer−metal complexes involving one or two carboxylate groups resulting in charge reversal or charge annihilation.