On the Calcium Binding Mechanisms of Acacia Gums (senegal and seyal): importance of solvation in the binding process

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The pronounced Ca^{2+}-binding capacity of acacia gum leads to both desirable and undesirable attributes in food applications, underscoring the need to understand its binding mechanism. We quantitatively characterized interactions between Ca^{2+} and demineralized *A. senegal* and *A. seyal* gums using dual-electrode potentiometric titration, isothermal titration calorimetry (ITC), and quartz crystal microbalance with dissipation (QCM-D). Potentiometric titration revealed clear pH dependence, with maximal Ca^{2+} binding capacities of 12.7 and 13.4 mg·g^{-1} at pH 7.0 (approximately one Ca^{2+} per two carboxyl groups) for *A. senegal* and *A. seyal* , respectively, and steadily decreasing binding toward pH 3.0. Ca^{2+} association triggered pronounced proton release at pH 5.0, due to binding-induced reductions in the pK_{obs} of glucuronic acids (GlcA). ITC showed moderate binding affinities (K_a in the range of 10^3-10^4 M^{-1}) and positive apparent enthalpies (deltaH $_{obs}$), possibly indicating entropy-driven dehydration that masks intrinsic exothermic complexation. DH $_{obs}$ of *A . senegal* was significantly higher than that of *A. seyal* due to their distinct GlcA and/or 4-O-Me-GlcA profiles. Measurements at lower pH and across buffers demonstrated that deltaH $_{obs}$ variations were governed by proton exchange and buffer protonation enthalpy rather than purely electrostatic attraction. Despite the large amount of bound Ca^{2+} , few inter-macromolecular associations of Acacia gums were observed upon Ca^{2+} binding. The results provide new insights into the formulation design of Acacia gum, as well as into the physicochemical basis of cation association in plant AGPs.