# CHARGED POLYSACCHARIDES AS MODEL POLYELECTROLYTES: COMPUTATIONAL STUDIES OF TRANSPORT AND CONFORMATIONAL PROPERTIES

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# Abstract

Homogalacturonans (HGs) are polysaccharide co-polymers of galacturonic acid and its methylesterified counterpart, that play a crucial role in the mechanobiology of the cell walls of all land plants. When extracted, in solution, at pH values above the pKa, the carboxyl groups carried by the unmethylesterified residues endow the polymer chains with charge, making these systems interesting polyelectrolytes. The inter- and intra-molecular distributions of the non-charged methylesterifed residues and their charged unmethylesterifed counterparts are vital behaviour-determining characteristics of a sample's structure. Previous work has led to the development of techniques for the control of the amount and distribution of charges, and with these tools and samples available in different degrees of polymerisation, including small oligomers, the system offers a flexible test-bed for studying the behaviour of biological polyelectrolytes.

This thesis is rooted in exploring the use of computational approaches, in particular molecular dynamics, to calculate the conformation of such polyelectrolytes in solution and to describe their transport properties in electric fields. The results of simulations are, in all cases, compared with the results of experimental work in order to ground the simulations.

First, in chapter 2, these simulations are applied to calculate the free solution electrophoretic mobilities of galacturonides, charged oligosaccharides derived from digests of partially methylesterified HGs. The simulations are compared with experiment and were found to correctly predict the loss of resolution of electrophoretic mobilities for fully-charged species above a critical degree of polymerisation (DP), and the ionic strength dependence of the electrophoretic mobilities of different partially charged oligosaccharides.

Next, in chapter 3, molecular dynamics (MD) simulations are used to calculate the electrophoretic mobilities of HGs that have different amounts *and distributions* of charges placed along the backbone. The simulations are shown to capture experimental results

well even for samples that possess high charge densities. In addition they illuminate the role that *local* counterion condensation can play in the determination of the electrophoretic mobility of *heterogeneous* blocky polyelectrolytes that cannot be adequately described by a single chain-averaged charge spacing.

Finally, in chapter 4, the last part of the research focusses on the configurations of these polyelelectrolyes in dilute solution, and on how the interactions between several chains can lead to the spatially heterogenous nature of polyelectrolyte solutions. Such questions are of long standing interesting in the polyelectrolyte field and the results are compared with results from Small Angle X-Ray Scattering(SAXS).

Overall the work demonstrates how state of the art MD approaches can provide insights into experimental results obtained from fundamentally interesting and biologically relevent polyelectrolytes.

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