INFLUENCE OF ANOMERIC CONFIGURATION AND GLYCOSIDIC LINKAGE ON THE SOLUTION CONFORMATIONAL ENTROPY OF OLIGOSACCHARIDES

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We often refer to size-exclusion chromatography (SEC) as an entropically-driven technique, without giving the matter much thought. However, if it is true that separation in SEC is due to an entropic difference between phases, it stands to reason that SEC should then be able to provide entropic information about analytes. There are some restrictions on obtaining this type of information, however: Analytes must be perfectly monodisperse and enthalpic contributions to the separation must be virtually absent. The first requirement restricts this application of SEC to oligomers and select biopolymers, as all synthetic polymers possess some degree of polydispersity. Here, we show how SEC using a single concentration-sensitive detector can be used to measure the solution conformational entropy of oligosaccharides. Anomeric configuration and glycosidic linkage are shown to individually affect the flexibility of various oligosaccharide series under aqueous, quasi-physiological conditions of temperature and pH. Chromatographic results have been augmented by calculations using molecular dynamics computer modeling methods and the influence, or lack thereof, of enthalpic contributions to the separation has also been addressed.