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Molecular dynamics simulation study of the association modes between calcium and polygalacturonate

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ABSTRACT

Polygalacturonic acid (polyGalA) is the main component of pectin, a natural polysaccharide that is often used as a gelling agent in food and pharmaceutical industries. The ionotropic gelation of polyGalA involves the formation of ionic bridges between the carboxylate groups of polyGalA chains mediated by divalent cations such as calcium and is usually described by the popular "egg-box model" [1]. In this study [2], we performed molecular dynamics (MD) simulations to investigate the various association modes between Ca^{2+} and polyGalA. To this aim, we first slightly revised the empirical parameters for the interaction between Ca^{2+} and the carboxylate oxygen atoms of GalA units, so as to reproduce the experimental Ca^{2+}-GalA association constant (Figure 1a). Biased MD simulations using these revised parameters indicate that, in the most favored configurations of Ca^{2+}-polyGalA complexes (Figure 1b), both the number of GalA-Ca^{2+}-GalA ionic bridges (NB) formed between polyGalA chains and the local coordination geometry of bound Ca^{2+} differ from those proposed by the egg-box model, which thus fails to describe accurately the association modes between calcium and polyGalA.

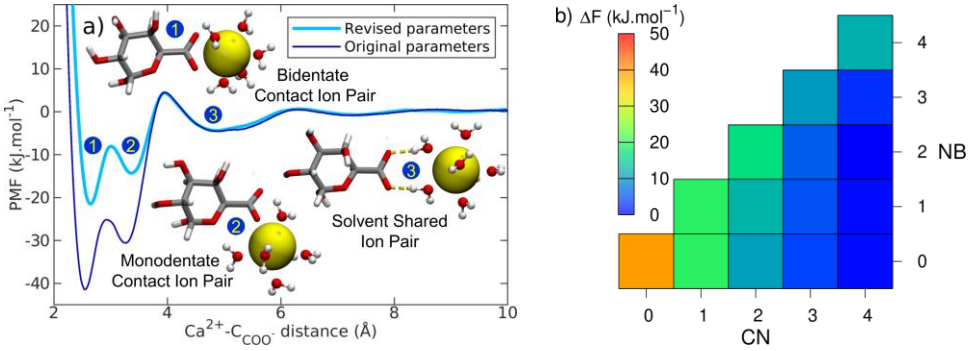

Figure 1. a) Potentials of mean force (PMF) for the Ca^{2+}-GalA interaction using the revised and the original force field parameters. Instantaneous configurations for the bidentate contact ion pair (CIP) (1), monodentate CIP (2), and solvent shared ion pair (SSIP) (3) coordination modes obtained using the revised parameters are also shown. b) Free energy profile, ΔF, as a function of the number of calcium cations bound to the polyGalA chains (CN) and the number of GalA-Ca^{2+}-GalA ionic bridges formed between the polyGalA chains (NB) determined from a bias-exchange metadynamics (BEMD) simulation.

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