MEDIATING ROLE OF ALKALINE EARTH METAL IONS IN ELECTROSTATICS OF DNA: THE LONG-RANGE EFFECTS OF SOLVENT DIELECTRIC SATURATION

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The epsilon-modified Poisson-Boltzmann (ε-MPB) equations [1,2] have been solved on a three-dimensional grid for an all-atom geometry model of B-DNA [1,3]. Results were obtained for the models of one and two DNAs in solutions of chlorides of alkali and alkaline earth metals and their mixtures. The ε-MPB approach is based on the primitive polarization model (PPM) of electrolyte [4] that is an implicit solvent model including finite sizes of hydrated ions and a dielectric approximation of the ion hydration shell. All PPM parameters approximating dielectric medium and hydration shells of ions were extracted from all-atom molecular dynamics simulations of ions in SPC/E water [2,4-6]. The study allows evaluations of the ion size, interionic correlation, and solvent dielectric saturation effects on the ion distributions around DNA and DNA-DNA interaction energies. It suggests that the dielectric saturation of the ion hydration shell drastically affects distributions of alkaline earth metal ions around DNA, resulting in high affinity of calcium or magnesium ions to the phosphate groups of DNA. As follows from the ε-MPB calculations, the dielectric saturation of the ion hydration shells leads to decrease of the mean permittivity around DNA, compensating the DNA-DNA attraction arising from interionic correlations. As a result, two DNA macromolecules in solution of $MgCl_2$ or $CaCl_2$ repel each other in accordance with experimental data. Calculations for B-DNA in a mixture of NaCl and $MgCl_2$ solutions suggest that adding a tiny fraction (1 mM) of Mg^{2+} drastically affects DNA-DNA interaction energies [1]. Even in this case the peculiar polarization properties of the cluster $[Mg(H_2O)_6]^{2+}$ lead to sharp condensation of Mg^{2+} onto phosphates of DNA and notably affect the mean force acting between two DNA macromolecules. Calculated ionic distributions around DNA and DNA-DNA interaction energies agree with previously published simulations and experimental data.

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References

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