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F1

Structure of Water and Counterions in DNA

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Monte Carlo simulation have been performed to study the hydration of two DNA conformers: the right-handed B-DNA and the left-handed Z-DNA, both in the double helix conformation. The models used to represent the polyelectrolytes consist of three full pitches (60 and 72 nucleotides units for B- and Z-DNA, respectively).

The simulations have been carried out at a temperature of 300 K with 500 water molecules per pitch and as many counterions as necessary to neutralize DNA. In the present studies three different monocharged counterions have been considered: Li^+, Na^+ and K^+. During the Monte Carlo process either the water molecules or the counterions are subject to displacements [1].

The Monte Carlo walks, for these six simulations, have been analyzed in such way to give, for the counterions, information about their position (not yet determined by experiments), and the number of water molecules in their first hydration shell. Some of the counterions have, in the first hydration shell, the same number of water molecules as determined for the same ion in solution [2], but some other lose one or even two water molecules and complete their coordination by binding DNA atoms. There is a preference for the three kind of ions here analyzed, to bind either the PO_4^- groups or the N7 atoms in guanine and adenine [3].

The water structure in the first hydration shell of the DNA is analyzed for specific sites (for example for the nitrogen or the oxygen atoms at the bases) or for groups of sites (for example the bases or the PO_4^-). For both DNA conformers, the polyelectrolyte loses water from the first hydration shell if K^+ is replaced with Na^+ or Na^+ with Li^+.

As known in B-DNA, there are two grooves, the minor and major. The water was found to be highly structured in both grooves. In the minor groove there is either a long filament of water molecules running along the groove or small filaments connecting two phosphate groups belonging to the same strand. In the major groove the water molecules form filaments connecting phosphate groups belonging to two different strands [4]. The first and the last type of filaments are stable for a sufficiently long time as to be detected by X-ray diffraction, as shown recently [5].

These results have been obtained performing, for each of the six simulations, 10^6 displacements (after equilibration). As known, after each displacement the interaction energy of the system, namely, the interaction energy between water–DNA, water–ions, ion–ion, ion–DNA and water–water is computed. In the present study the interaction energies are calculated with potentials obtained by fitting thousands of *ab initio* computations [6]; for the water–water the MCY potential [7], obtained from Configuration Interaction computations, has been used.

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F2

Ion Transport through Membranes: A Computer Experiment

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Gramicidin-A is a linear pentadecapeptide antibiotic, which forms transmembrane channels; these have a number of interesting conductance characteristics [1, 2 and Refs. therein], as for example high specific ion fluxes (a single channel carries about 10^7 sodium ions/sec at 25 °C, 1 *M* NaCl and 100 mV transmembrane d.d.p.) and have a remarkable ion