Impact of nanopore's topology on the electrical double layer and capacitance

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The electrolyte structure inside and outside of nanopores immersed into a bulk electrolyte is analytically obtained [1]. Three different nanopore topologies are studied, i.e., planar, cylindrical, and spherical. The nanopores are model as nanocavities of wall thickness, d, with equal surface charge density, σ_0, on both surfaces of the nanopores. The electrolyte is model as a point-ion symmetrical electrolyte, at a given concentration, ϱ_0. The dielectric constant of the fluid and the nanopores are taken to be equal to avoid image potentials. The nanopores are considered as electrodes, not directly connected to a power source. The electrical double layer inside and outside the nanopores are attained through the analytical solution of the corresponding linearized Poisson-Boltzmann equation. Thus, analytical formulas for the mean electrostatic potential, electrolyte's reduced concentration, and electrical field profiles, are exhibited. In particular, analytical expressions for the nanopore's differential capacitances are presented. The nanopores are treated as permeable, so the electrolyte outside and inside the electrodes are at the same chemical potential. Analogous analytical formulas for solid nano-electrodes are obtained as a corollary of those for nanopores. In particular, their analytical expressions for the differential capacitance here derived are shown to be consistent with the capacitive compactness proposed in the past by one of us [2]. Numerical results of all of the above functions are analyzed as a function of the nanopores geometrical parameters and the electrolyte's temperature and molar concentration. It is found that the spherical topology, at lower temperatures, has the higher differential capacitance. It is demonstrated that for the three nanopore topologies here considered their capacitances reduce to that of a single planar electrode, in the limit of infinitely wide nanopores. The electrical double layer and mean electrostatic potential of the three topologies are in qualitatively agreement with those from the non-linearized Poisson-Boltzmann, hypernetted chain/mean-spherical approximation (HNC/MSA) equations and computer simulations results presented in the past, within the low mean electrostatic potential assumption. Connection of nanopore capacitance with biological, chemical and medical systems is briefly discussed.

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