Modelling ion transport to charged surfaces: Dynamics of electric double layer formation

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Introduction. Ion transport plays an important role in many self-organization processes such as crystal growth, periodic precipitation, formation of colloid particles, biological morphogenesis, and many others. The ionic flows are driven by gradient in both chemical and electric potentials and the resulting behavior is usually complex showing nonlinearities in time and space.

Theory. The ion fluxes obey the Nernst-Planck (NP) equation $J_i = -D_i \left(\nabla c_i - \frac{z_i F}{RT} c_i \nabla \varphi \right)$

where D_i, c_i, and z_i are diffusion coefficient, molar concentration, and charge number of i-th ion, respectively and F, R, T stand for Faraday constant, gas constant, and absolute temperature. The spatial profile of electric potential φ is given by the Poisson equation

$$\nabla^2 \varphi = -\frac{\rho}{\varepsilon}$$ where ρ is charge density and ε permitivity.

Methods. Applying the continuity equation, a set of time-dependent PNP equations describing electrodiffusion in a solution of uni-univalent electrolyte was solved by the method of lines with adaptive grid and variable time step (VLUGR2 solver for a 2D problem). Both the Gouy-Chapman (GC) and Gouy-Chapman-Stern (GCS) models of electric double layer (EDL) were employed. The initial and boundary conditions for a sudden voltage step or charge injection at the left boundary were specified as follows:
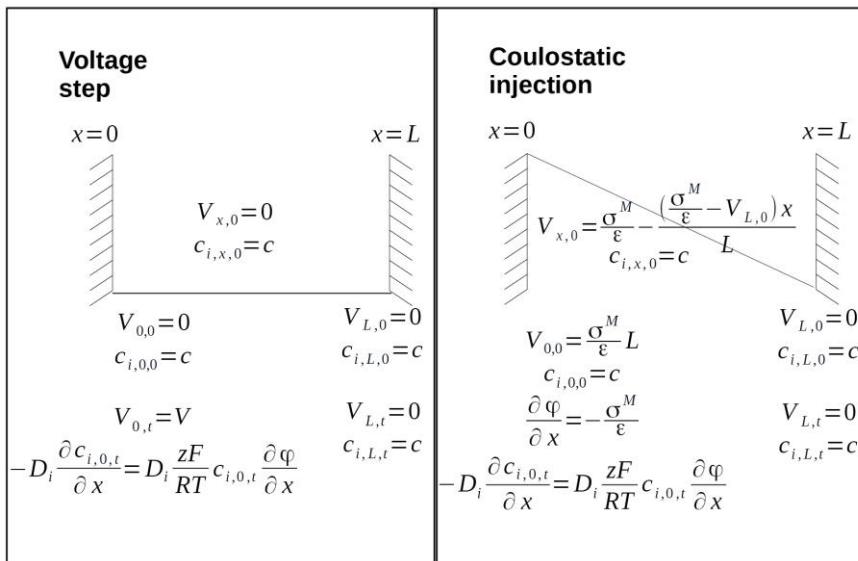
Results. Simulated dynamics of the EDL formation is shown in Figure 1. The steady state profiles are in good agreement with theoretical predictions for the diffuse EDL (GC theory).
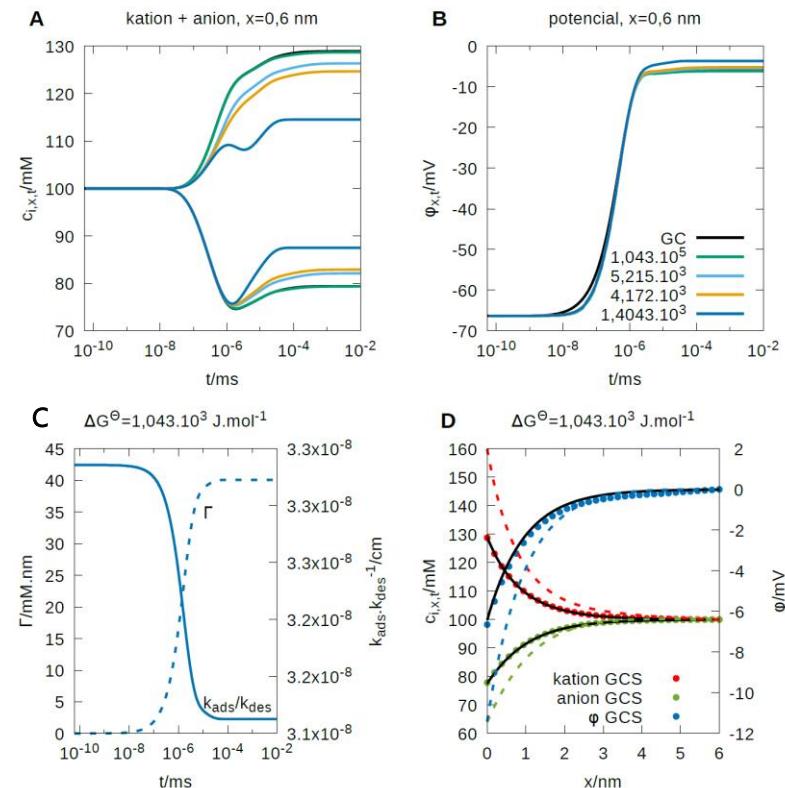
Figure 1. Evolution of EDL after coulostatic injection (σ^M = -8.54 mC m^{-2}) for various desolvation energies (ΔG^Θ) of the cation.
A: concentrations of cations (upper lines) and anions; **B**: electric potential; **C**: surface concentration of cations (dashed line); **D**: spatial profiles of ion concentrations and electric potential in the steady state (dashed lines for the GC model).