Poisson-Boltzmann Equations

The Poisson-Boltzmann equations can be used for computing the 1-D distribution of ions near a wall of fixed voltage. We assume a binary symmetric electrolyte where only positive C^+ and negative C^- species with valence one. We consider the dimensionless version of the equations, where the concentration of ions is normalized to the bulk concentration far away from the wall, the potential is normalized to the thermal voltage $kT/e = 25mV$, and the length is normalized by the Debye length $\lambda^2 = (\epsilon RT)/(2F^2 z^2 c_0)$. At steady state, the divergence of the flux of each species must be zero,

$$\frac{\partial}{\partial x}\left(\frac{\partial C^+}{\partial x} + C^+\frac{\partial \phi}{\partial x}\right) = 0 \tag{1}$$

$$\frac{\partial}{\partial x}\left(\frac{\partial C^-}{\partial x} - C^-\frac{\partial \phi}{\partial x}\right) = 0, \tag{2}$$

where ϕ is the electric potential. The flux is composed of molecular diffusion and electro-migration. If there are no chemical reactions, the ionic flux must be zero at the wall, $x = 0$. If there is no flux at the wall, the governing equations state that the flux everywhere must be zero. This means the equations are reduced to,

$$\frac{\partial C^+}{\partial x} = -C^+\frac{\partial \phi}{\partial x} \tag{3}$$

$$\frac{\partial C^-}{\partial x} = C^-\frac{\partial \phi}{\partial x}. \tag{4}$$

To close the system we use Gauss's law for the electric potential, given that the difference in C^+ and C^- is the charge density,

$$2\frac{\partial^2 \phi}{\partial x^2} = C^- - C^+. \tag{5}$$

The factor of two results from the scaling by the Debye length.

Integration of equation 3 and 4 yields

$$C^+ = e^{-\phi} \tag{6}$$

$$C^- = e^{\phi} \tag{7}$$

and substituting into Gauss's law yields

$$\frac{\partial^2 \phi}{\partial x^2} = \sinh(\phi). \tag{8}$$

When the applied potential at the wall is small, this equation is easily solved to yield,

$$\phi = Ve^{-x} \tag{9}$$

where V is the applied voltage at the wall.

For arbitrary voltage this equation may still be solved analytically, but we will not present the solution here. In the MATLAB function `pb.m` we present a way to solve these equations numerically using MATLAB's features for boundary value problems. An even simpler implementation would solve Equation 8 using MATLAB and then use Equations 6 and 7 for the concentration. We do not adopt that approach as we wish to demonstrate the solution of a system of equations for a model problem.

When solving equations 3, 4, and 5 we need 4 boundary conditions. They are $\phi(x = 0) = V$, $\phi(x = \infty) = 0$, $C^+(x = \infty) = 1$, and $C^-(x = \infty) = 1$. Since we cannot use an infinite domain, we simply take the x direction to be large enough such that the finite domain makes no difference on the solution.