Mathematical model for the concentration and electric potential profiles in a solution of electrolytes under a redox reaction

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Outline

Diffusion Of Electrolytes In Aqueous Solution

Steady State Solution

Dynamic solution

Diffusion Of Electrolytes In Aqueous Solution

Diffusion equation with external electric field

- The problem of diffusion

$$\frac{\partial C_s}{\partial t}(x,t) + \nabla \cdot \mathbf{N}_s(x,t) = 0.$$

- Electric potential due to charge distribution (electrolytes)

$$\nabla^2 \phi = -\frac{\rho(x,t)}{\epsilon \epsilon_0}.$$

Here ϵ is water's permittivity and ϵ_0 the permittivity of free space. $s = \pm$.

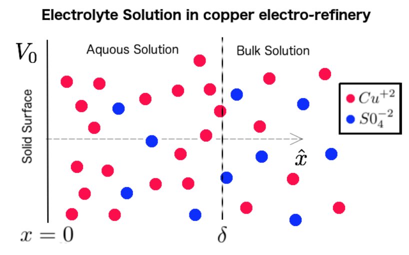


Figure 1

Mathematical model of the flux

Model for the flux of electrolyte

$$\mathbf{N}_s = -D_s \left(\nabla \cdot C_s(x)_+ + s \frac{zF}{RT} C_s(x) \nabla \phi(x) \right)$$

It is convenient to work with the dimensionless potential $\Psi = \frac{zF}{RT}\phi$

$$\mathbf{N}_s = -D_s \left(\nabla \cdot C_s(x)_+ + s C_s(x) \nabla \Psi(x) \right)$$

The charge distribution is given by the concentration of each electrolyte on every point of the solution times its electrical charge.

$$\rho(x,t) = \sum_{s=\pm} szFC_s(x,t)$$

Mathematical model of the system

Dimensionless length parameter $\xi = \kappa x$ Infinitely large plate implies

$$\nabla_\xi^2 \to \frac{\partial^2}{\partial \xi^2}$$

. With these considerations, the equations take the form

$$\frac{\partial C_+}{\partial t}(\xi, t) = -D_+ \nabla^2 C_s(\xi) - \nabla(C_+(\xi)\nabla\Psi(\xi, t)), \tag{1}$$

$$\frac{\partial C_-}{\partial t}(\xi, t) = -D_- \nabla^2 C_s(\xi) + \nabla(C_-(\xi)\nabla\Psi(\xi, t)), \tag{2}$$

$$\frac{\partial^2 \Psi(\xi, t)}{\partial \xi^2} = -\frac{\kappa^2}{C_b}\left(C_+(\xi, t) - C_-(\xi, t)_-\right). \tag{3}$$

where $\kappa^2 = \frac{(zFC_b)^2}{RT\epsilon_r\epsilon_0}$ and C_b the bulk concentration.

Border conditions

The border conditions for this problem can be obtained looking at figure 2

- $(\partial C_+/\partial t + \nabla \cdot \mathbf{N}_+)\big|_{interface} = r,$
- $(\partial C_-/\partial t + \nabla \cdot \mathbf{N}_-)\big|_{interface} = 0,$
- $C_+ = C_- = C_b,$
- $\Phi(0) = \frac{zFV_0}{RT} = \Phi_0$,
- $\Phi(\delta) = 0$.

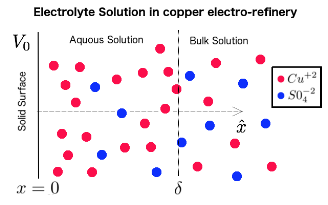


Figure 2

Steady State Solution

Steady state approach

As a first approach to solving the system, we compute the steady state solution.

$$\frac{\partial C_+}{\partial t}(\xi, t) = 0 \Rightarrow \nabla \cdot \mathbf{N}_+ = 0 \qquad \Rightarrow \mathbf{N}_+(\xi)\big|_{surface} = r, \tag{4}$$
$$\frac{\partial C_-}{\partial t}(\xi, t) = 0 \Rightarrow \nabla \cdot \mathbf{N}_- = 0 \qquad \Rightarrow \mathbf{N}_-(\xi)\big|_{surface} = r, \tag{5}$$

which yields the following system of equations for the steady state problem

$$\nabla C_+(\xi) - C_+(\xi)\nabla\Psi(\xi) = r, \tag{6}$$
$$C_-(\xi) + C_-(\xi)\nabla\Psi(\xi) = 0, \tag{7}$$
$$\nabla^2\Psi(\xi) = -\kappa^2\left(C_+(\xi) - C_-(\xi)_-\right). \tag{8}$$

By means of a perturbation analysis with r as a control parameter we obtain solve the previous system up to first order in r. The zero order solution is

$$\Phi^{(0)}(\xi) = 2\log\left(\tanh\left(\frac{\xi-\xi_0}{2}\right)\right), \tag{9}$$

Where

$$C_s^{(0)}(x) = C_{b,s}e^{s\Phi^{(0)}(x)}$$

Perturbative solution of the system

In order to solve the system to first order in r, the following approximation was made.

$$\left|\frac{\partial \phi^{(1)}}{\partial x}\right| << \frac{\kappa V_0}{r}, \tag{10}$$

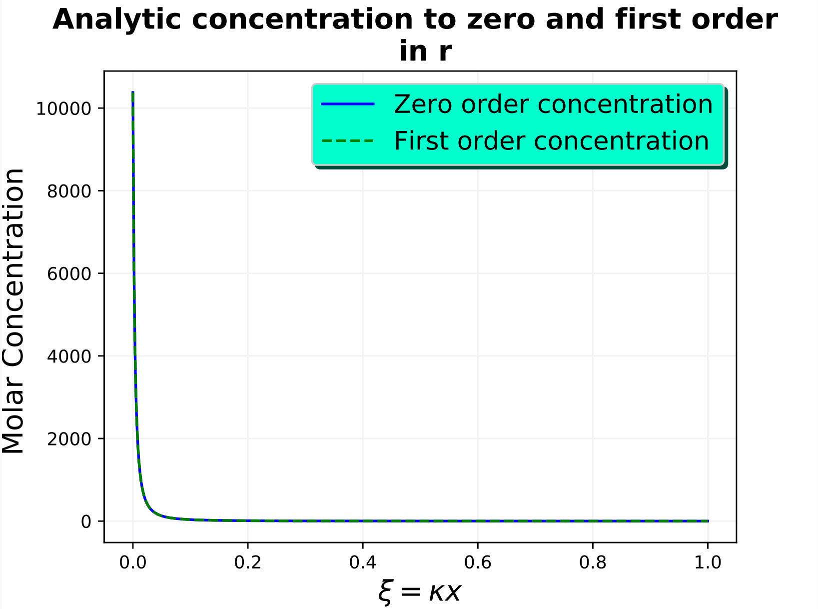
Which yields

$$C_+^{(1)}(\xi) = \quad -\frac{1}{\kappa} e^{-\Phi^{(0)}(\xi)} \left(\xi - 2\left(\tanh\left(\frac{\xi - \xi_0}{2}\right) + \tanh\left(\frac{\xi_0}{2}\right)\right)\right),$$

and

$$C_-^{(1)}(\xi) = 0. \tag{11}$$

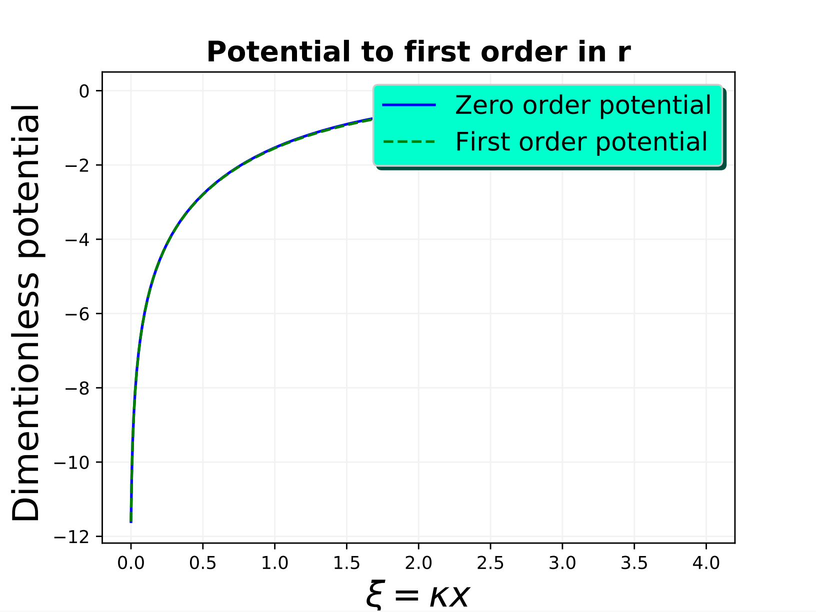
Analytic results for the concentration



The first order term in the potential expansion is

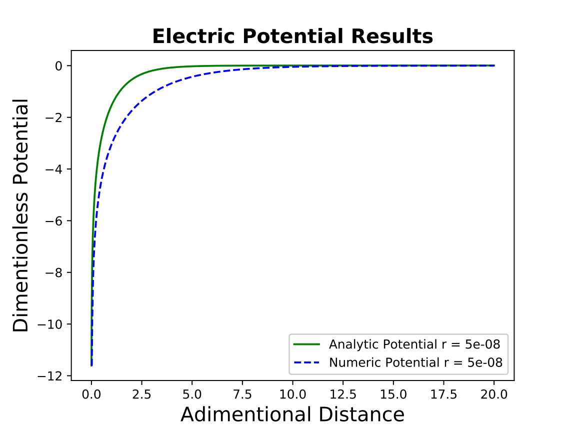
$$\Phi'^{(1)}(\xi) = \frac{1}{\kappa}\left(\frac{1}{2}\xi^2 - 2\gamma\xi + 2(2\gamma - \xi)\coth\left(\frac{\xi - \xi_0}{2}\right)\right) + C$$
$$C = -\frac{1}{\kappa}\left(\frac{1}{2}\xi_\delta^2 - 2\gamma\xi_\delta + 2(2\gamma - \xi_\delta)\coth\left(\frac{\xi_\delta - \xi_0}{2}\right)\right).$$

Analytic results for the potential



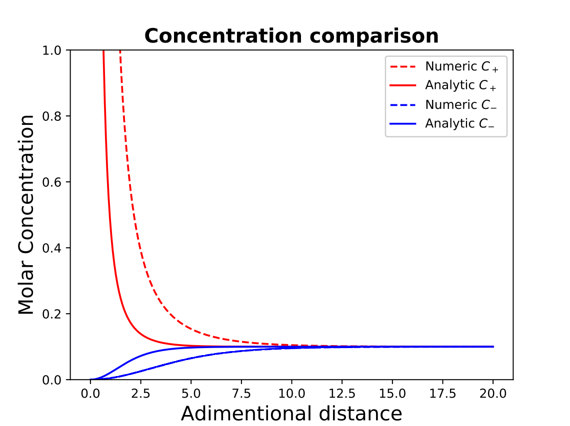
Numeric Results

For numeric computation the Runge-Kutta of fourth order was used. The following graph shows a comparison between the numeric an analytic system for $r = \kappa \times 10^{-5} \approx 2.28$.



Numeric Results

The following graph shows a comparison between the numeric an analytic concentrations.



Dynamic solution

Stage of the project

We are currently working on solving the complete problem, including the dynamics.

$$\frac{\partial C_+}{\partial t}(\xi, t) = -D_+ \nabla^2 C_s(\xi) - \nabla(C_+(\xi) \nabla \Psi(\xi, t)), \qquad (12)$$

$$\frac{\partial C_-}{\partial t}(\xi, t) = -D_- \nabla^2 C_s(\xi) + \nabla(C_-(\xi) \nabla \Psi(\xi, t)), \qquad (13)$$

$$\frac{\partial^2 \Psi(\xi, t)}{\partial \xi^2} = -\frac{\kappa^2}{C_b} \left(C_+(\xi, t) - C_-(\xi, t)_- \right). \qquad (14)$$

To-do list

1. Finish numerical computation of the dynamical system
2. Include stochastic reaction rate to measure noise
3. Couple to NV-center.