# ELECTROSTATIC INTERACTIONS BETWEEN POLYELECTROLYTES WITHIN AN ULTRACENTRIFUGE

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## Abstract
We characterize electrostatic and other polymer-polymer interactions within an ultracentrifuge cell using a new electrochemical transport model. Applying conservation of mass and momentum of solutes and solvent, and Maxwell's equations valid in the electroquasistatic (EQS) limit, together with initial and boundary conditions on solute (and electrolyte) distribution, we predict the transient (nonequilibrium) and equilibrium solute (and electrolyte) distributions, net charge density, electric field, and electrostatic potential profiles. This model represents a significant advance over the Lamm equation (and its extensions) [1], which describe polymer-polymer interactions phenomenologically (using empirical virial coefficients) [2].

## Introduction
The behavior of polyelectrolyte solutions and gels, colloids, and tissues is affected by electrostatic interactions between charged molecules. Within an ultracentrifuge cell, we can titrate these media--subjecting them to a known, spatially varying mechanical force distribution. However, a large disparity exists between theoretical and measured concentration profiles in many polymeric solutions, which has been ascribed to non-ideal interactions [2], such as electrostatic repulsion and excluded volume, which have been modeled phenomenologically.

## Equations Governing Solute Transport
The flux of solute i in the radial direction, $\Gamma_r(r,t)_i$, is given by a Nernst/Planck equation:

$$\Gamma_r(r,t)_i = S_i c_i \omega^2 r - D_i \frac{\partial c_i}{\partial r} + \gamma_i \frac{z_i}{|z_i|} c_i E_r$$

where $S_i$ is the Svedberg sedimentation coefficient, $\gamma_i$ is the electrical mobility, $D_i$ is the diffusion coefficient, $\omega$ is the rotor angular velocity, $z_i$ is the solute valence, $c_i(r,t)$ is the solute concentration, and $E_r(r,t)$ is the radial component of the *macroscopic* electric field. All variables are functions of the radial coordinate r and of time t.

Continuity for each solute within the cell is:

$$\frac{\partial c_i(r,t)}{\partial t} = - \nabla \bullet \Gamma_i + G(r,t)_i - R(r,t)_i$$

where $G(r,t)_i$ and $R(r,t)_i$ are the rates of production and removal of species i, respectively (e.g., $H^+$).

We use Maxwell's equations for charged particles in solution [3] to determine $E_r$. The net (ionic) current flux, $J_r(r,t)$, is:

$$J_r(r,t) = \sum_{i=1}^{N} J_r(r,t)_i = F \sum_{i=1}^{N} z_i \Gamma_r(r,t)_i$$

In the centrifuge, the net charge per mole of solvent is negligible, so that the appropriate form of the equation of charge continuity is:

$$\frac{\partial \rho_{free}(r,t)}{\partial t} \approx 0 = \nabla \bullet J = \frac{1}{r} \frac{\partial}{\partial r} \left( r\, J_r(r,t) \right)$$

implying that the initial macroscopic charge distribution will be preserved during the experiment.

## Boundary Conditions
We require that no current flows across the solvent/air (r=a) and solvent/cell (r=b) boundaries:

$$J_r(a,t) = J_r(b,t) = 0$$

Therefore, we can express $E_r$ explicitly in terms of $c_i$, its gradient, and other experimental parameters:

$$E_r = - \frac{RT}{F} \frac{\sum_{i=1}^{N} z_i \left( S_i \omega^2 c_i r - D_i \frac{\partial c_i}{\partial r} \right)}{\sum_{i=1}^{N} D_i z_i^2 c_i} ,$$

providing closure to the transport model.

## Initial Conditions
Initially we assume that all mobile species are well mixed (uniformly distributed) within the cell.

$$c_i(r,0) = c_{i_0} ,$$

and that the initial macroscopic charge distribution satisfies the bulk electroneutrality condition:

$$\rho_{free}(r,0) = F \sum_{i=1}^{N} z_i c_{i_0} = 0 .$$

Taken together with the equation of charge conservation, bulk electroneutrality is satisfied for all t and r within the centrifuge cell.

## Numerical Methods

The governing equations and the boundary conditions are coupled, non-linear partial differential equations that we solved numerically for each $c_i$ in the transient and steady-state cases, using a finite-element method. The steady-state case was solved using the constraint that the total mass of each species within the ultracentrifuge cell is conserved.

## Results/Model Predictions

Numerical solutions were obtained for a large uncharged solute (MW=70 kDa), for a charged, non-dissociable solute in a binary electrolyte (NaCl). By including additional transport equations for $[H^+]$ and $[OH^-]$, and an equilibrium dissociation isotherm of acidic and basic charged groups of the solute, we obtained its concentration profiles in a binary aqueous electrolyte as well as profiles of $[H^+]$ and $[OH^-]$. From the concentration profiles for all mobile species, $c_i(r,t)$, we calculated $\rho_{free}(r,t)$, $E_r(r,t)$, and the electrostatic potential $\phi(r,t)$ over a wide range of ionic strength (0.0001M-1.0M), and rotor angular velocity, $\omega_f$, (0 - $2000\pi$ sec$^{-1}$). Figure 1 shows the concentration profile for an uncharged solute.

## Discussion

The model predicts the correct qualitative behavior in all important limiting cases under equilibrium and nonequilibrium conditions. For example, when $E_r=0$, the governing equations reduce to the familiar Lamm equations. However, unlike the Lamm equation, the system of electrochemical transport equations, and the (no-flux) boundary conditions are generally inextricably coupled because $E_r$ acts on *each* charged solute molecule while it is produced by the distribution of *all* charged molecules. Consequently, linear non-equilibrium thermodynamic analysis [4] may not be sufficient to describe this coupling without also applying Maxwell's equations.

While previously unreported, the model predicts that co- and counter-ion distributions may vary with r in colloidal and polyelectrolyte solutions, because the charged solute is distributed non-uniformly. The pH may also vary between the inner and outer boundaries at the highest rotor RPM. This phenomenon may be important in ligand binding and thermodynamic studies of charged molecules, even at physiological ionic strength.

Normalizing the governing equations yields the dimensionless Peclet number for each solute,

$$Pe_i = \frac{S_i \omega^2 (b-a)^2}{D_i} ,$$

a transport parameter that affects steady-state concentration profiles, the time it takes to achieve them, and the scaling of results obtained in different ultracentrifugation experiments.

We have considered polyelectrolyte systems in which the dominant non-ideal interaction is electrostatic, however the model can be extended to incorporate other nonideal interactions.

## Conclusion:

This formalism describes electrochemical transport of charged and uncharged macromolecules in an ultracentrifuge cell, allowing electrostatic and other interactions to be included self-consistently, while obviating the use phenomenological virial coefficients. The model also predicts distributions of electrolytes, (e.g., $[OH^-]$, $[H^+]$, $[Na^+]$, or $[Cl^-]$) that we may not choose to or be able to measure. The electrochemical transport model also can be exploited to estimate non-equilibrium transport parameters, such as molecular mobility.
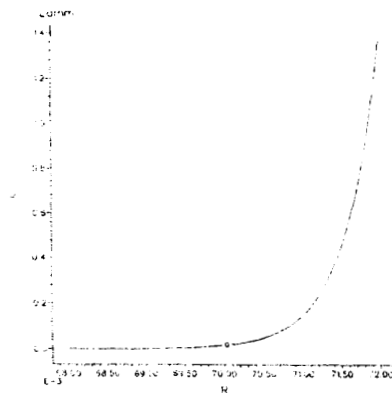


Fig. 1. Concentration profile for uncharged solute.

## References

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