Monte Carlo simulation of a model nanopore sensor: device behavior emerging from ion competition

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Introduction

The alkali and different metal ions play a key role in today’s raw material policy. Therefore, in the case of recycling of wastage, new methods for detection are needed. One possible solution are sensors fabricated of nanopores with the basic operational concept of detecting the presence of these ions qualitatively and quantitatively. By placing binding sites on the nanopore’s wall which are selective for one of these ions (analyte, X⁺ or X⁺⁺), the binding of the analyte creates a change in the current flowing through the nanopore, thus, the presence of the analyte can be detected through this current-modulation. We present a modeling study which examines the effects of experimentally controllable parameters on the device behavior. Through these parameters (voltage and background electrolyte concentration) current-voltage and calibration curves can be obtained to determine the concentration of the analyte.

Results

Current-voltage (I-V) curves
- The main charge carrier is Cl⁻ due to the left positive zone of the pore.
- The presence of various analyte concentrations modulates the shape of the I-V curves differently.
- Unknown analyte concentration is determinable from the shape of the I-V curve.
- The pore rectifies due to charge asymmetry.
- The mechanism of X detection is that more X attracts more Cl⁻ into the pore thus.

Calibration curves and rectification
- On lower cKCl increasing cX attracts more Cl⁻ and repulses more K⁺, the shape of the calibration curve is monotonic.
- Competitive effect: higher cKCl gives higher ICl⁻ while increasing cX extrudes K⁺ from the pore, creating an extremum in the calibration curve.

Concentration profiles
- As cX increases, X ions attract more Cl⁻ ions into the pore.
- At cX = 0.01 M, K⁺ ions are excluded from the left hand side, so K⁺ current is absent.
- At cX = 0.1 M, K⁺ ions are present, but this (K⁺) leakage vanishes with as more X ion appears in the pore. This causes the maximum in the I/I₀ curve.

Model

- Ions: Charged hard spheres (Primitive Model of electrolytes)
- Solvent: implicit water. Ions are immersed in a dielectric continuum of dielectric constant ε = 78.5.
- Binding sites: Square-well potential. The short-range potential attracts X with εKCL energy once the closest point of the X ion’s surface is closer to the site than the distance parameter dKCL:

\[ \mu_{\text{KCl}}[n] \xrightarrow{\text{LEMC}} c_{\text{KCl}}[n] \rightarrow \mu_{\text{KCl}}[n+1] \]

The whole system is solved in an iterative scheme until conservation of mass (\( \nabla \cdot j_i(r) = 0 \)) is satisfied.

Method

Nernst-Planck equation

\[ j_i(r) = \frac{1}{kT} D_i(r) c_i(r) \nabla \mu_i(r) \]

jᵢ is the flux density of ionic species, k is the Boltzmann’s constant, T is temperature, cᵢ is the concentration profile, \( \mu_i(r) \) is the electrochemical potential profile.

The relation between \( c_i(r) \) and \( \mu_i(r) \) is established with Local Equilibrium Monte Carlo (LEMC) simulation. The computation domain of the NP system is divided into volume elements with different \( \mu_i \) values.

NP + LEMC method

Conclusion

This modeling study presents an option for recognition of ions with different valences. Through the examination of the effects of experimentally controllable parameters, deductions for molecular mechanisms inside the pore can be made.

1. Through the usage of an asymmetric charge pattern on the nanopore’s wall, the analyte and the surface charge together modulate the current of the main charge carrier ion (Cl⁻).
2. Higher cKCl leads to a leakage of K⁺ ions through the pore which creates an extremum in the calibration curve, thus lower cKCl is preferable.

This model sensor is able to detect the analyte ions in low concentrations. Using NP+LEMC methodology it is possible to handle finite size of ions and ionic correlations at the same time with reasonable computational time.

References


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