Scaling in uniformly charged and bipolar nanopores through a modified Dukhin number

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Nanopores

- Natural (ion channels) and artificial pores in a membrane

**Input parameters:**

- **Nanopore fabrication:** radius \( R \), length \( H \), surface charge \( \sigma \)
- **Experimentally controllable:** electrolyte concentration in bulk \( c \), voltage \( U \), ionic valences \( z_i \)

**Output (measurable) parameters:**

- electric currents \( I_+ \), \( I_- \), particle currents \( J_+ \), \( J_- \), \( I_i = z_i e J_i \)

**Device function:**

- In the case of uniformly charged nanopores is the selectivity:
  \[
  S_+ = \frac{|J_+| - |J_-|}{|J_+| + |J_-|}
  \]

- For bipolar nanopores the rectification:
  \[
  \text{ICR} = \frac{I_{\text{ON}} - I_{\text{OFF}}}{I_{\text{ON}} + I_{\text{OFF}}}
  \]
Model and methods

- Nernst-Planck equation:
  \[ j_i(r) = -\frac{1}{kT} D_i(r) c_i(r) \nabla \mu_i(r) \]

- Relationship between concentration profile \((c_i(r))\) and chemical potential profile \((\mu_i(r))\) is computed with
  - Local Equilibrium Monte Carlo⁻ → LEMC+NP
  - Poisson-Boltzmann theory → PNP

- Water: implicit

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Scaling means that the device function, $F$, is an analytical function of a (dimensionless) scaling parameter, $\xi$:

$$F = f[\xi(a_1, a_2, a_3 \ldots)]$$

**Practical importance**: if we have a scaling parameter, $\xi$, for a given combination of $a_1, a_2, \ldots$, we can predict the device function for another combination, $a'_1, a'_2, \ldots$, giving the same $\xi \rightarrow$ nanopore design

For a nanopore, the input parameters ($a_i$) are $R, c, \sigma, \ldots$

But what is the scaling parameter, $\xi$?
Dukhin number as a scaling parameter?

- The Dukhin number originally describes the ratio of surface and volume conductances (Bikerman, Lyklema, Dukhin)
- Bocquet’s definition\(^a\):
  \[ \text{Du} = \left| \frac{\sigma}{ecR} \right| \]
- For 1:1 electrolytes, we rewrite Du as
  \[ \text{Du}^0 = \left| \frac{\sigma 8\pi l_B \lambda_D^2}{eR} \right| \]
  where \( l_B = e^2/(4\pi \epsilon_0 \epsilon kT) \) is the **Bjerrum-length** and
  \[ \lambda_D = \left( \frac{ce^2}{\epsilon_0 \epsilon kT} \sum_i z_i^2 \nu_i \right)^{-1/2} \]
  is the **Debye-length**

Double layer behavior controls device behavior (selectivity)

- The overlap of the double layers is **controlled** by $\lambda_D/R$.
- The cation-anion separation near the wall is **controlled** by $\sigma$.
- Large $\sigma$ and strong overlap $\rightarrow$ high selectivity.
- Small $\sigma$ and weak overlap $\rightarrow$ low selectivity.
- Selectivity can be tuned by these parameters.

![Graph showing selectivity across different values of $\lambda_D/R$ and $\sigma$](image)

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Nanopore geometries: from nanotube to nanohole

- Nanotube limit: PET nanopores
- Nanohole limit: graphene nanopores
Nanotube \((H \to \infty)\) limit – The Dukhin number is an appropriate scaling parameter

- \(S^+\) vs. \(\lg Du^0\): sigmoid curve
- The inflection point belongs to selectivity \(S^+ \approx 0.5\) serving as a transition point separating "rather non-selective" and "rather selective" regions.
- Extension to multivalent electrolytes:
  \[
  Du = \frac{(z^+ + |z^-|) Du^0}{2 + (z^+ - |z^-|) Du^0}
  \]
- For 1:1 electrolytes: \(Du = Du^0\)
- See poster # 28 of Valiskó et al.
Du is **not** an appropriate scaling parameter for finite pores

If we start decreasing the pore length, the double layers at the entrances of the pore “penetrate” into the pore and modify the ionic distributions inside the pore.

The curves are shifted to the right, so shorter pores require larger surface charges to produce the same selectivity.

The shift of the curves and thus the scaling can be characterized by the inflection point ($Du_{infl}$)
The derivation of the modified Dukhin number (mDu)

- $\lambda_D/H$-dependence of the inflection point
- The blue line shows a linear fit to the nanohole ($H \to 0$) limit
- If we divide the $Du$ by this $Du_{infl}$, the inflection point "stay in place"
- The modified Dukhin number: $mDu = Du/(\lambda_D/H)$ is an appropriate scaling parameter for finite long pores.
mDu is an appropriate scaling parameter for finite pores

The advantage of the mDu parameter is that it contains $H$ so it can account for the length of the pore.

\[
mDu = Du \frac{H}{\lambda_D} = \frac{|\sigma|8\pi l_B \lambda_D H}{eR}
\]

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The device function is the ionic current rectification

\[ \text{ICR} = \frac{I^\text{ON} - I^\text{OFF}}{I^\text{ON} + I^\text{OFF}} \]

where \( I^\text{ON} = I(U) \) and \( I^\text{OFF} = I(-U) \).

Diode behavior
Concentration profiles: the role of depletion zones

- Depletion zones are formed for the cations in the $\sigma$ region, and for the anions in the $-\sigma$ region.

- The basis of the mechanism of rectification is that the OFF voltage makes the depletion zones deeper compared to the ON state.

- Changing the sign of the voltage from ON to OFF results in reduced concentrations inside the pore.
The bipolar nanopores are necessarily of finite length due to their charge pattern, so the modified Dukhin number can be used as a scaling parameter.

Voltage is taken into account by

$$mDu' = mDu \frac{U}{U_0}$$
Summary

What is good in scaling?
Prediction
If you know the device behavior for some experimentally attainable combinations of the input parameters, you can deduce a master curve and you can predict the device behavior for any combinations.
Reducing problems and analyzing mechanisms.
Focusing on basic physics.
Deviation from scaling indicates the importance of strong molecular correlations.
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