A THEORETICAL MODEL OF STREAMING POTENTIAL AND ZETA POTENTIAL IN ROCKS

Paul Glover & Emilie Walker
Université Laval, Québec, Canada

Matthew Jackson
Imperial College, London, UK
The classical Helmholtz-Smoluchowski equation relates the streaming potential coupling coefficient (SPCC) to:

- Zeta potential
- Pore fluid dielectric permittivity
- Pore fluid conductivity
- Pore fluid viscosity

Developed for capillary tubes

Commonly applied to rocks

However, never been validated for rocks (no measure of zeta potential)

Never even been a theoretical model applied to real rocks

**DESPITE** most of the theoretical tools being available since 1998
In this presentation:

Development of the required theoretical tools

Compilation of a SPCC dataset for rocks

Compilation of a zeta potential dataset for rocks

Modelling SPCC of rocks as a function of salinity

Modelling $\zeta$ of rocks as a function of salinity
Database

SPCC vs. Pore fluid salinity
Silica, glass, sand and sandstone 11 sources

Acknowledgments to Jaafar (2009)
Zeta potential vs. Pore fluid salinity
Silica, glass, sand and sandstone
7 sources

Acknowledgments to Jaafar (2009)
The method is as follows:

1. Calculate the pore fluid conductivity (salinity and temperature)

   \[ \sigma_f(T, C_f) = \left( d_1 + d_2 T + d_3 T^2 \right) C_f - \left( \frac{d_4 + d_5 T}{1 + d_6 C_f} \right) C_f^{3/2} \]

   Sen and Goode (1992)

2. Calculate the pore fluid relative permittivity (salinity and temperature)

   \[ \varepsilon_f(T, C_f) = \varepsilon_o \left( a_0 + a_1 T + a_2 T^2 + a_3 T^3 + c_1 C_f + c_2 C_f^2 + c_3 C_f^3 \right) \]

   Olhoeft (1980)

3. Calculate the pore fluid viscosity (salinity and temperature)

   \[ \eta_f(T, C_f) = e_1 + e_2 \exp(\alpha_1 T) + e_3 \exp(\alpha_2 C_f^m) + e_4 \exp(\alpha_3 T + \alpha_4 C_f^m) \]

   Phillips et al. (1978)
4. Define the physical chemistry of the double layer

\[ \frac{K_{(-)}}{K_{Me}} \]

\[ > \text{SiOH}^0 \iff > \text{SiO}^- + \text{H}^+ \]

\[ > \text{SiOH}^0 + \text{Me}^+ \iff > \text{SiOMe}^0 + \text{H}^+ \]

5. Calculate or set the pore fluid pH (SiO\textsubscript{2}-H\textsubscript{2}O-CO\textsubscript{2})

\[
C_H^3 - (C_a - C_b)C_H^2 - (K_w + K_1)C_H^1 - 2K_1K_2 = 0
\]

\[ K_w = 6.9978 \times 10^{-16} + 5.0178 \times 10^{-16}T - 2.4434 \times 10^{-17}T^2 + 7.1948 \times 10^{-19}T^3 \]

Lide (2009); Revil et al. (1999)

6. Calculate the Debye screening length and shear plane distance

\[ \chi_d = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_b T}{2000N e^2 I_f}} \quad \text{and} \quad I_f = \frac{1}{2} \sum_{i}^{n} Z_i^2 C_i^f \]

\[ \chi_\zeta = 2.4 \times 10^{-10} \text{ m} \]
7. Calculate the Stern plane potential

\[ \phi_d = \frac{2k_b T}{3e} \ln \left( \frac{\sqrt{8 \times 10^3 \varepsilon_r \varepsilon_o k_b T N} (10^{-pH} + K_M e C_f)}{2e \Gamma_s K_\varepsilon} \right) \left[ \frac{C_a + C_b + C_f + 10^{-pH}}{\sqrt{I_f}} \right] \]

Revil and Glover (1997; 1998)

8. Calculate the zeta potential

\[ \zeta = \phi_d \exp \left( -\chi_\zeta / \chi_d \right) \]

Revil and Glover (1997; 1998)
9. Calculate the surface conductance \( \Sigma_s = \Sigma_s^{EDL} + \Sigma_s^{Prot} + \Sigma_s^{Stern} \)

\[
\Sigma_s^{Stern} = \frac{e\beta_s \Gamma_s^o K_M e C_f}{10^{-pH} + K_-} \left( \frac{\sqrt{8 \times 10^{-3} \varepsilon_r \varepsilon_o k_b T N \left( 10^{-pH} + K_M e C_f \right)}}{2e\Gamma_s^o K_-} \right)^{2/3} + K_M e C_f
\]

\[
\Sigma_s^{EDL} = R \left( B_{Na^+} C_f + B_{H^+} 10^{-pH} \right) \left( S \left( \frac{10^{-pH} + C_f K_M e}{2e\Gamma_s^o K_-} \right)^{-1/3} - 1 \right) + \left( B_{Cl^-} C_f + B_{OH^-} 10^{pH-pK_f} \right) \left( S \left( \frac{10^{-pH} + C_f K_M e}{2e\Gamma_s^o K_-} \right)^{1/3} - 1 \right)
\]

\[
R = \sqrt{\frac{2 \times 10^{-3} \varepsilon_r \varepsilon_o k_b T N}{C_f + 10^{-pH}}}
\]

\[
S = \sqrt{8 \times 10^{-3} \varepsilon_r \varepsilon_o k_b T N \left( C_f + 10^{-pH} + 10^{pH-pK_w} \right)}
\]

Revil and Glover (1997; 1998)
10. Calculate the SPCC

\[ C_s = \frac{\Delta V}{\Delta P} = \frac{d \varepsilon_f \zeta}{\eta_f \left( d \sigma_f + 4 \sum_s m F \right)} \]

- Fundamental constants \((k_b\text{ and } N_A\text{ etc.})\).
- Environmental conditions \((T\text{ etc.})\).
- Fluid parameters (salinity, \(pH\), \(pK_w\), \(pK_1\) \text{ and } \(pK_2\) etc.).
- Rock microstructure parameters \((F, m, \phi, d\text{ etc.})\).
- Rock-fluid interface parameters, i.e., the electro-chemical parameters associated with surface adsorption reactions \((pK_{me}, pK_{-}\text{ etc.})\).

Glover and Déry (in press)
# Theoretical model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value or range</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>25</td>
<td>°C</td>
<td>Experimental condition</td>
</tr>
<tr>
<td>Pore fluid salinity</td>
<td>$C_f$</td>
<td>$10^{-5} - 3.98$</td>
<td>mol/L</td>
<td>Varied between limits</td>
</tr>
<tr>
<td>Pore fluid pH</td>
<td>$pH$</td>
<td>6 - 8</td>
<td>(-)</td>
<td>Varied between limits</td>
</tr>
<tr>
<td><strong>Fundamental constants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dielectric permittivity in vacuo</td>
<td>$\varepsilon_o$</td>
<td>$8.854 \times 10^{-12}$</td>
<td>F/m</td>
<td>Lide (2009)</td>
</tr>
<tr>
<td>Boltzmann’s constant</td>
<td>$k_b$</td>
<td>$1.381 \times 10^{-23}$</td>
<td>J/K</td>
<td>Lide (2009)</td>
</tr>
<tr>
<td>Charge on an electron</td>
<td>$e$</td>
<td>$1.602 \times 10^{-19}$</td>
<td>C</td>
<td>Lide (2009)</td>
</tr>
<tr>
<td>Avagadro’s number</td>
<td>$N$</td>
<td>$6.02 \times 10^{23}$</td>
<td>/mol</td>
<td>Lide (2009)</td>
</tr>
<tr>
<td><strong>Fluid parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Added acid concentration</td>
<td>$C_a$</td>
<td>variable</td>
<td>mol/L</td>
<td>Calculated from pH</td>
</tr>
<tr>
<td>Added base concentration</td>
<td>$C_b$</td>
<td>variable</td>
<td>mol/L</td>
<td>Calculated from pH</td>
</tr>
<tr>
<td>Surface mobility</td>
<td>$\beta_s$</td>
<td>$5 \times 10^{-9}$</td>
<td>m²/s/V</td>
<td>Revil and Glover (1997)</td>
</tr>
<tr>
<td>Reaction constant carbonisation</td>
<td>$pK_1$</td>
<td>7.53</td>
<td>(-)</td>
<td>Wu et al. (1991)</td>
</tr>
<tr>
<td>Reaction constant dehydrogenisation</td>
<td>$pK_2$</td>
<td>10.3</td>
<td>(-)</td>
<td>Wu et al. (1991)</td>
</tr>
<tr>
<td>Parameter</td>
<td>Symbol</td>
<td>Value or range</td>
<td>Units</td>
<td>Reference</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>--------</td>
<td>----------------</td>
<td>-------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td><strong>Rock parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grain size (diameter)</td>
<td>$d$</td>
<td>$2 \times 10^{-4}$</td>
<td>m</td>
<td>St Bee's SST (Jaafar et al., 2009)</td>
</tr>
<tr>
<td>Cementation exponent</td>
<td>$m$</td>
<td>1.86</td>
<td>(-)</td>
<td>Calculated $m = -\log F / \log \phi$</td>
</tr>
<tr>
<td>Formation factor</td>
<td>$F$</td>
<td>19.80</td>
<td>(-)</td>
<td>St Bee's SST (Jaafar et al., 2009)</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\phi$</td>
<td>0.19</td>
<td>(-)</td>
<td>St Bee's SST (Jaafar et al., 2009)</td>
</tr>
<tr>
<td><strong>Rock/fluid interface parameters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface site density</td>
<td>$\Gamma_s^o$</td>
<td>$1 \times 10^{+19}$</td>
<td>sites/m²</td>
<td>Adjusted to fit data</td>
</tr>
<tr>
<td>Binding constant for cation (sodium) adsorption on quartz</td>
<td>$pK_{me}$</td>
<td>7.1</td>
<td>(-)</td>
<td>Adjusted to fit data</td>
</tr>
<tr>
<td>Disassociation constant for dehydrogenisation of SiOH</td>
<td>$pK_{(-)}$</td>
<td>7.5</td>
<td>(-)</td>
<td>Adjusted to fit data</td>
</tr>
<tr>
<td>Shear plane distance</td>
<td>$\chi_\zeta$</td>
<td>$2.4 \times 10^{-10}$</td>
<td>m</td>
<td>Revil and Glover (1997)</td>
</tr>
<tr>
<td>Surface conduction (protonic)</td>
<td>$\Sigma_s^{Prot}$</td>
<td>$2.4 \times 10^{-9}$</td>
<td>S</td>
<td>Revil and Glover (1997)</td>
</tr>
<tr>
<td>Surface mobility</td>
<td>$\beta_s$</td>
<td>$5 \times 10^{-9}$</td>
<td>m²/s/V</td>
<td>Revil and Glover (1997)</td>
</tr>
</tbody>
</table>
SPCC vs. Pore fluid salinity
Silica, glass, sand and sandstone
3 different pHs
4 different grain sizes
General properties of the SPCC database and absolute values are well described
Grain size can be extremely important
Zeta potential vs. Pore fluid salinity

Silica, glass, sand and sandstone

3 different pHs

Database measurements are very scattered

Highly sensitive to changes in pH
Individual modelling suggests that the operating pH is low (about pH 5.5).
Compiled: A database of SPCC vs. pore fluid salinity for silica-based rocks

Compiled: A database of zeta potential vs. pore fluid salinity for silica-based rocks

Developed: A method for modelling the SPCC and zeta potential of porous media as a function of pore fluid salinity

Theoretical model: Shows systematic variations with pH and grain size

Using whole database: The theoretical approach is capable of describing the general properties of the database as well as the absolute values of SPCC and zeta potential

Using individual rocks: The theoretical approach is capable of describing some of the fine structure apparent in the individual SPCC and zeta potential determinations as a function of salinity
This work has been made possible thanks to funding by the

**Natural Sciences and Engineering Research Council of Canada (NSERC)**

*Discovery Grant Programme*