Debye–Hückel Theory

\[
\mathcal{U}(r_{ij}) = \frac{q_i q_j}{4 \pi \varepsilon r_{ij}}
\]

\[
\varepsilon_r = 78 \ (H_2O \leftrightarrow 298 \ K)
\]

Energy of ion \(i\)

\[
\mathcal{U}_i = \frac{\sum q_i q_j}{4 \pi \varepsilon r_{ij}}
\]

"Field" description

\[
\nabla^2 \Phi(r) = \frac{-\mathcal{P}(r)}{\varepsilon}
\]

Poisson's Equation

\[
\mathcal{P}(r) = e \mathcal{P}_+(r) - e \mathcal{P}_-(r)
\]

\[
\mathcal{P}(r) = \text{charge density}
\]

In spherical coordinates,

\[
\nabla^2 \Phi(r) = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \Phi}{dr} \right) = -\frac{\mathcal{P}(r)}{\varepsilon}
\]

→ Assumes "smeared out" charges with continuous distribution that depends only on \(r\)

How does \(\mathcal{P}_+ \), \(\mathcal{P}_-\) differ from \(\mathcal{P}_b\), their mean (bulk) values?

\[
\frac{\mathcal{P}_-(r)}{\mathcal{P}_b} = \exp \left( -\frac{\mathcal{U}_-}{k_b T} \right) = \exp \left( +\frac{e \Phi(c)}{k_b T} \right) \quad \text{(Canonical ensemble probabilities)}
\]

\[
\frac{\mathcal{P}_+(r)}{\mathcal{P}_b} = \exp \left( -\frac{e \Phi(c)}{k_b T} \right) \quad \text{(Boltzmann factors)}
\]
Combining \([1] - [3]\)
\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \Phi(v)}{dr} \right) = - \frac{1}{\varepsilon} \left[ q_+ p_+(v) + q_- p_-(v) \right] \]

\[
= - \frac{e \rho_b}{\varepsilon} \left[ \exp \left( - \frac{e \Phi(v)}{k_B T} \right) - \exp \left( + \frac{e \Phi(v)}{k_B T} \right) \right]
\]

\(\text{(assumed monovalent co/solvent ions)}\)

For dilute solutions, we can linearize this equation by Taylor expansion:

\[
\exp \left( - \frac{e \Phi(v)}{k_B T} \right) \approx 1 - \frac{e \Phi(v)}{k_B T} \quad \text{e+t.c. to obtain}
\]

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d \Phi(v)}{dr} \right) = \frac{2 e \rho_b}{\varepsilon k_B T} \quad \Phi(v) = k^2 \Phi(v) \quad [4]
\]

\(k^{-1}\) is the Debye length

\[
k^2 = \frac{1}{\varepsilon k_B T} \sum \frac{q_i^2 \rho_i}{\varepsilon_i}
\]

\(k^2\) is proportional to the Ionic Strength of the solution:

This 2\(\text{nd}\)-order ODE takes solutions of the form:

\[
\Phi(v) = c_1 \exp[kr] + c_2 \exp[-kr] \quad r > a
\]

\[
\Phi(v) = c_1 \frac{\exp[kr]}{r} + c_2 \frac{\exp[-kr]}{r} \quad r > a
\]

Boundary Conditions: \(\Phi(v) \to 0 \quad \text{as} \quad r \to \infty \Rightarrow c_1 = 0\)

For \(c_2\), we first need to get the "inner potential"

\[
\Phi(v) \quad r < a
\]
\[ \frac{d^2(\varphi(r))}{dr^2} = 0 \quad \text{inside central ion} \]

\[ \Rightarrow \varphi(r) = C_3 + \frac{C_4}{r} \quad r < a \]

\[ \uparrow \quad \uparrow \quad \text{constant effect of central charge} \]

\[ C_4 = \frac{Q}{4\pi\varepsilon} \quad \text{since central charge has magnitude} \quad +Q \]

\[ C_3, C_2 \text{ can be obtained from:} \]

\[ \varphi(a) \text{ must be continuous} \]

\[ \Rightarrow \frac{d\varphi}{dr} \text{ at } r = a \]

\[ \frac{d\varphi}{dr} \text{ must be continuous} \]

\[ C_3 + \frac{Q}{4\pi\varepsilon a} = C_2 \frac{\exp(-ka)}{a} \]

\[ -\frac{Q}{4\pi\varepsilon a^2} = -C_2 \frac{(1+ka)\exp(-ka)}{a^2} \]

\[ \text{Solving:} \quad C_2 = \frac{Q \exp(ka)}{4\pi\varepsilon (1+ka)} \]

\[ C_3 = -\frac{Q}{4\pi\varepsilon} \left( \frac{ka}{1+ka} \right) \]

\[ \rho(r > a) = -\varepsilon \nabla^2 \varphi(r) = \]

\[ = -\frac{Q k^2 \exp(-k(r-a))}{4\pi r (1+ka)} \quad \text{(some steps skipped)} \]

The potential is

\[ \varphi(r > a) = \frac{Q}{4\pi\varepsilon} \cdot \frac{\exp(-k(r-a))}{1+ka} \]
The potential around the central ion is screened: at small distances looks like \( \frac{Q}{4\pi \varepsilon r} \) at long \( r \) decays exponentially. Electrostatic screening is the reason electrolyte solutions have extensive thermodynamic properties.

\[ \text{Gibbs free energy} \]

Take the limit for \( a \to 0 \), small central ions:

\[
\Psi_i (r > 0) = \frac{Q_i \cdot e^{-kr}}{4\pi \varepsilon r} = \frac{Q_i}{4\pi \varepsilon r} - \frac{Q_i k}{4\pi \varepsilon r} = \Psi_{\text{cloud}} - \Psi_{\text{counterion cloud}} \]

Self potential of central ion:

\[ \text{Work for changing central ion:} \]

\[
d\omega_{ei} = \Psi_{\text{cloud}} dQ_i = -\frac{k}{4\pi \varepsilon} Q_i dQ_i \Rightarrow
\]

\[ \omega_{ei} = -\frac{kQ_i^2}{8\pi \varepsilon} \]

\[ k_i = k_{\text{id}}, i + k_{\text{ei}} \Rightarrow m_{\text{ei}} = k_i - k_{\text{id}}, i = k_B T \ln \Psi_i \]

\[ \ln \Psi_i = -\frac{kQ_i^2}{8\pi \varepsilon k_B T} \]

Recall that \( K^2 \) is proportional to \( I = \sum q_i^2 \rho_i \)
For monovalent salts, \( I = 2 \rho \frac{\text{mol salt}}{\text{volume of solution}} \)

Deviations from DH become significant above \( \approx 0.1 \text{ M for } 1:1 \text{ electrolytes,} \)
\( \approx 0.01 \text{ M for } 2:1 \)

At higher \( \rho \) deviations because of

- excluded volume of ions
- ion-ion interactions
- change in \( E \) of the solution