The electric double-layer

- With a charged surface, there must be a solution in contact that contains ions of equal and opposite charge.
- The charge of a surface can be measured by its electric potential (volts).
- If the surface has variable charge, this potential changes with a change in pH.

Helmholtz double layer

- Simple model that contains two planes.
- One plane = charged surface
- Second plane = layer of adsorbed ions
- No other ions present
  - e.g. if the surface is negative, the counter ions are cations in a single layer
- The charge potential drops linearly with distance from the surface.
- Does not work for soils—charged surfaces are not strong enough to adsorb a monolayer.

The diffuse double layer

Diffusive forces (thermal motion) move cations away (and anions towards)

Electrostatic forces attract cations (and repulse anions)

negatively charged surface

Higher cation concentration in towards surface. Higher anion concentration away from surface

Gouy Chapman DDL theory

$$c_x = c_B \exp(-ZF\psi_d/RT)$$

- The concentration of an ion at x distance from the surface = the concentration in the bulk solution times a bunch of constants (F, R, T), ionic charge (Z) and potential (ψ_d) at x distance.

$$\psi_d = \psi_o \exp(-\kappa x)$$

$$\kappa = \mathbf{Z}F\ (2\ \mathbf{I}\ 10^3\ /\ \text{constants})^{0.5}$$

- The potential at any distance from the surface is a function of ionic charge (Z) and ionic strength (I)

Constant vs. variable charge

- In a constant charge system (e.g. clays with permanent charge from isomorphic substitution), higher molarity (ionic strength) and ionic charge will decrease the thickness of the double layer.
- In a variable charge system, higher ionic strength and charge will also increase the charge.

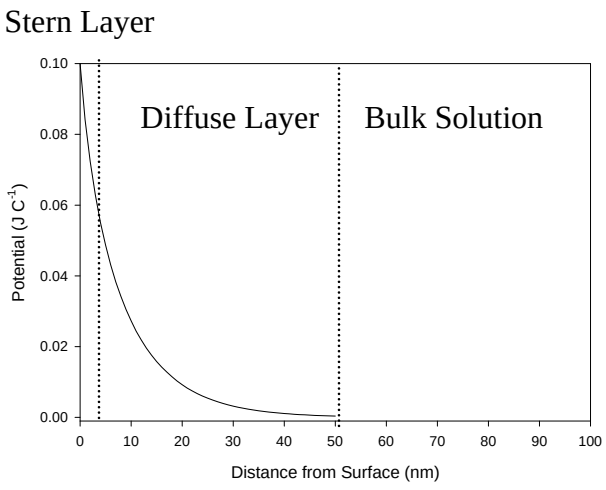
Assumptions of the Guoy-Chapman Model

- Only electrostatic interactions occur
  - i.e. no inner-sphere bonding with surface
- The counterions behave as “point” charges
  - ie. they have no size
- Counterions all are in a diffuse cloud
  - Not realistic, Stern theory corrects
- The properties of the bulk water are the same as the water next to the surface
  - Not realistic, dielectric constant changes

Stern

- Gouy-Chapman predicts an unrealistically high concentration of ions close to the surface.
- Stern added a layer that is between the surface and the diffuse cloud.
- Results in a more realistic calculation of surface potential or surface charge

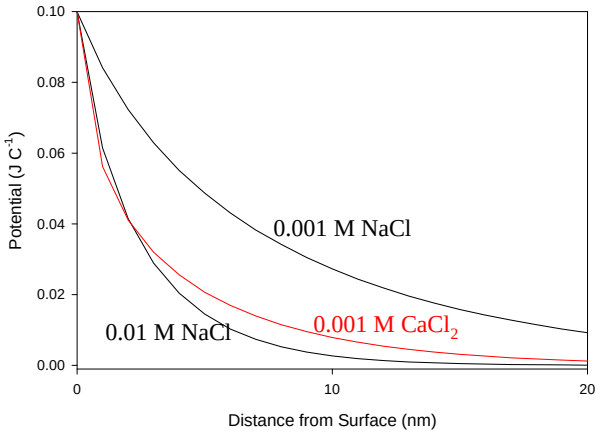
Gouy-Chapman / Stern



DDL theory

- What can it tell you / explain?
  - Flocculation / dispersion
    - 25-150 mmolar for monovalent ions
    - 0.5-2.0 mmolar for divalent
    - 0.01-0.1 for trivalent
  - Swelling
  - How they are affected by:
    - charge of cation
    - concentration of cation

Gouy-Chapman



Surface complexation models

- DDL models do not allow surface complexes
- A series of models have been developed that do allow inner-sphere surface sorption.
- Surface charge is the sum of:
  - permanent (constant vs. changes in pH or I)
  - net proton charge (result of H^+ dissociation)
  - inner-sphere complex charge (charge remaining on sorbed ligands or metals)
  - outer-sphere complex charge