

In many systems from charged membrane separations to electrokinetic flows, the behavior of ions in aqueous media plays a crucial role. There are a number of elective courses avail. dedicated to this topic - here we will just look at some of the basics.

The starting point is Maxwell's Equations for the electric field in a vacuum:

$$\epsilon_0 \nabla \cdot \underline{E} = \rho^{(e)} ; \nabla \times \underline{E} = 0$$

$\rho^{(e)}$   $\equiv$  electric charge/volume

$\epsilon_0$   $\equiv$  permittivity of the vacuum

$\underline{E}$  is the electric field vector

If we apply this to a spherical volume containing total charge  $Q$

we get  $\vec{E} = \frac{Q}{4\pi\epsilon_0 r^3} \vec{r}$

so the electric field (like gravity!) goes as  $\frac{1}{r^2}$ . If you have two charges  $Q_1$  &  $Q_2$  sep. by  $\vec{r}_{12}$  the force is:

$$\vec{F}_{12} = \vec{E}_1 Q_2 = \frac{Q_1 Q_2}{4\pi\epsilon_0 r_{12}^3} \vec{r}_{12}$$

Now because  $\vec{\nabla} \times \vec{E} = 0$  (irrotational) it must be represented as the gradient of a scalar (potential)

$$\vec{E} = -\vec{\nabla} \psi$$

Plugging this into Maxwell's eq'n we get:  $\epsilon_0 \nabla^2 \psi = -\rho^{(e)}$

so around an isolated charge  $Q$ :

$$\psi = \frac{Q}{4\pi\epsilon_0 r}$$

If you have a sphere of radius  $a$  and charge  $Q$ , the surface potential  $\psi_s$  is just  $\psi_s = \frac{Q}{4\pi\epsilon_0 a}$ .

This was for a vacuum. In a dielectric medium the capacitance ( $4\pi\epsilon_0 a$ ) increases due to polarization. This is due to orientation of permanent dipoles and deformation of electron clouds.

We define a polarization vector  $\vec{P}$  s. t.

$$\vec{P} = N \cdot Q \cdot \vec{d}$$

$\uparrow$  dipoles / vol       $\leftarrow$  distance & orientation of separation

$\swarrow$  charge separated to produce dipole

For a linear dielectric

$$\vec{P} = N \times \epsilon_0 \vec{E}$$

$\hookrightarrow$  polarizability of mat'l (units  $L^3$ )

The product  $N\alpha$  is the electric susceptibility of the material  $\chi \equiv N\alpha$

If we have a non-zero divergence of  $\underline{P}$  we get an effective charge! This is known as the polarization charge density

$$\rho^{(P)} : \quad \underline{\nabla} \cdot \underline{P} = -\rho^{(P)}$$

combining this with the total charge density we get:

$$\epsilon_0 \underline{\nabla} \cdot \underline{E} = \rho^{(e)}$$

$$\epsilon_0 \underline{\nabla} \cdot \chi \underline{E} = -\rho^{(P)}$$

$$\therefore \epsilon_0 \underline{\nabla} \cdot (1 + \chi) \underline{E} = \rho^{(e)} - \rho^{(P)} \equiv \rho^{(F)}$$

where  $\rho^{(F)}$  is the free charge density

Now if there are no free charges, then

$$\epsilon_0 \underline{\nabla} \cdot (1 + \chi) \underline{E} = 0$$

If we put a charged sphere in our dielectric there will be an effective polarization charge at the surface

which reduces the potential & electric field. Putting this together you get

$$Q = 4\pi\epsilon_0 (1 + \chi) a \psi_s$$

$\chi$ : dielectric constant of the material

What does this do?

- 1) For a given  $\psi_s$  (surface potential, voltage) it increases the charge (capacitance). That's why capacitors have high  $\epsilon$ !
- 2) For a given charge it reduces  $\psi_s$  and the electric field. This reduces the force between two charges by a factor of  $\epsilon$  too!

All this was for dielectrics w/ no free charge (e.g., no ions). In aqueous solutions ions respond to the electric field to produce a non-uniform dist.!

In an aqueous system, surfaces tend to acquire a charge! While this can be due to a different affinity for electrons or ionizable species it is often due to ionizable species that are bound to the surface: a sialic acid group on the surface of an RBC will ionize, leaving a bound negative charge. Proteins are usually amphoteric where amine groups will protonate (yielding + charge) or COOH groups will ionize (yielding - charge) depending on the pH!

At a charged surface in an electrolyte the counter ion will be attracted by the electric field, but will also diffuse away. This leads to the

"diffuse layer", we need to model this!

At equilibrium,

$$\epsilon \epsilon_0 \nabla^2 \psi = -\rho^{(F)}$$

For a particular ion  $\kappa$  the force on the ion balances the gradient in the chemical potential:

$$kT \nabla \ln n^\kappa + e z^\kappa \nabla \psi = 0$$

↑ Boltzmann's const.    ↑  $k$     ↑ # density of  $\kappa^{\text{th}}$  ion    ↑ electron charge    ↓  $\kappa$  charge (sign) of  $\kappa^{\text{th}}$  ion  
 $\nabla \psi \rightsquigarrow E$  (elec. field)

If we integrate this we get Boltzmann distribution:

$$n^\kappa = n_b^\kappa e^{-\left(\frac{e z^\kappa \psi}{kT}\right)}$$

where  $n_b^\kappa$  is the concentration where  $\psi = 0$

Now in your electrolyte you have at least two types of ions! The free charge density is the excess charge from the mixture. Thus:

$$\rho^{(f)} = \sum_i e z_i^{\kappa} n_i^{\kappa}$$

Putting this together, you get the Poisson-Boltzmann eq<sup>n</sup>:

$$\epsilon \epsilon_0 \nabla^2 \psi = -e \sum_i z_i^{\kappa} n_b^{\kappa} e^{-\left(\frac{e z_i^{\kappa} \psi}{kT}\right)}$$

This equation has the B.C. at the surface  $-\epsilon \epsilon_0 \nabla \psi \cdot \hat{n} = \rho$  where  $\rho$  is the surface charge density which is driving the non-uniform ion distribution.

Suppose we have a flat interface and a  $z-z$  electrolyte (e.g.,  $\text{Na}^+ \text{Cl}^-$ )



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our balance becomes:

$$\frac{d^2\psi}{dx^2} = \frac{2ez}{\epsilon\epsilon_0} n_b \sinh(ez\psi/kT)$$

If  $\frac{ez\psi}{kT} \ll 1$  (small potentials)

we get the Debye-Hückel approx:

$$\frac{d^2\psi}{dx^2} = \left( \frac{2e^2z^2n_b}{\epsilon\epsilon_0kT} \right) \psi$$

↳ units of  $\frac{1}{L^2}$

we can use this to define a Debye decay length (or double layer thickness)

$$\kappa^{-1} \equiv \left( \frac{\epsilon\epsilon_0kT}{2e^2z^2n_b} \right)^{1/2}$$

This is the length scale of the cloud of counter ions near a charged surface!

It is also the most important part

of this lecture! The key is the relationship between  $\kappa^{-1}$  and, say, pore radii. If you have a pore w/ fixed surface charges whose diameter is less than  $\kappa^{-1}$  then the surface charge modifies the ion distribution across the pore and you can get selective ion transport! If  $\kappa^{-1}$  is smaller than the pore diameter, the pore is unaffected (mostly) by the surface charge!

So how big is it?

$$\kappa^{-1} = \left( \frac{\epsilon \epsilon_0 kT}{2 e^2 z^2 n_b} \right)^{1/2}$$

Water:  $\epsilon = 80$  (dimensionless)

$$T = 298^\circ \text{K}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \frac{\text{F}}{\text{m}}$$

↘ Farad

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$$z = 1 \text{ (e.g., NaCl)}$$

$$k = 1.381 \times 10^{-23} \text{ m}^2 \text{ kg} / \text{s}^2 \text{ K}$$

OK, now for  $n_b$ : this is the salt concentration. Say we have a 0.01 M solution of NaCl:

$$n_b = 0.01 \frac{\text{moles}}{\ell} \times 1000 \frac{\ell}{\text{m}^3} \times 6.022 \times 10^{23}$$

(oh - and  $e = 1.602 \times 10^{-19}$  Coulombs)

So for these numbers:

$$k^{-1} = 3.07 \times 10^{-9} \text{ m} = 3 \text{ nm}$$

As an example, Prof Bruening's  $\text{Li}^+/\text{K}^+$  separation w/ 15 nm radius pores works fine at  $2 \times 10^{-4}$  M ionic strength, but fails at 0.2 M ionic strength. At  $2 \times 10^{-4}$  M (0.2 mM)  $k^{-1} = 22 \text{ nm}$ , greater than the pore radius. At 0.2 M

$\kappa^{-1} = 0.7 \text{ nm}$ , much less than the pore radius!

It is interesting that there is an exact solution to the potential without linearizing.

If we define  $\bar{\Psi} \equiv \frac{e z \Psi}{k T}$  (e.g., normalized)

we get:

$$\bar{\Psi} = 2 \ln \left( \frac{1 + e^{-\kappa x} \tanh\left(\frac{1}{4} \bar{\Psi}_s\right)}{1 - e^{-\kappa x} \tanh\left(\frac{1}{4} \bar{\Psi}_s\right)} \right)$$

$$\text{and } \rho = 2 \left( 2 \epsilon \epsilon_0 k T n_b \right)^{1/2} \sinh\left(\frac{1}{2} \bar{\Psi}_s\right)$$

Now if  $\bar{\Psi}_s$  is small, we get the linearized result. If  $\bar{\Psi}_s \gg 1$ , however,

$$\bar{\Psi} \sim 4 \tanh\left(\frac{1}{4} \bar{\Psi}_s\right) e^{-\kappa x}$$

away from the surface. since  $\tanh\left(\frac{1}{4} \bar{\Psi}_s\right) \rightarrow 1$  at large  $\bar{\Psi}_s$ , the

Potential and electric field <sup>382</sup> away from the surface behave as if there is a saturation potential  $\bar{\Psi}_s = \psi_0$  no matter how large the charge is!

All this is for a flat plate. If we have a colloidal particle it's usually a sphere of radius  $a$ ! The behavior depends on  $\kappa a$  - the ratio of the radius to the Debye length. If  $\kappa a \ll 1$  (say, a nano particle in a dilute electrolyte) then the force between two charged spheres is:

$$F \approx 2\pi\epsilon\epsilon_0 \left(\frac{kT}{ze}\right)^2 \kappa a \bar{\Psi}_s \frac{e^{-\kappa h}}{1+e^{-\kappa h}}$$

where  $h$  is the separation distance

If  $\kappa a \gg 1$  (usual case)

$$F \approx 32\pi\epsilon\epsilon_0 \left(\frac{kT}{ze}\right)^2 \kappa a \left[\tanh\left(\frac{\psi_0}{4\psi_s}\right)\right]^2 e^{-\kappa h}$$

The rapid decrease (exponential) w/  $Kh$  means that decreasing  $K^{-1}$  (e.g., increasing  $K$ ) reduces the force. Since  $K^{-1}$  goes as  $\frac{1}{n_b}^{1/2}$ , increasing salt concentration reduces electrostatic repulsion! That means adding salt to a colloidal suspension usually leads to aggregation as attractive short-range van der Waals forces take over!

Next lecture we'll look at what happens in an imposed electric field: electroosmosis & electrophoresis!