Charged interfaces

In polar solvents, most substances become charged:

- Preferential adsorption of ions.
- Dissociation of surface groups (ionization).
- Unequal ion dissolution.
- Ion replacement.
- Charged crystal surfaces.
Preferential ion adsorption

Which ions are preferentially adsorbed onto a particle?

- The ions composing the crystal (e.g. for AgCl: Ag\(^+\) and Cl\(^-\) ions)
- Ions forming sparingly soluble salts or strongly complexing ions with the crystal's ions (e.g. for AgCl: Br\(^-\) or SCN\(^-\))
- Multivalent ions (Ca\(^{2+}\), SO\(_4^{2-}\)) due to their high specific charge
- H\(_3\)O\(^+\) or OH\(^-\) ions (as they have a high mobility in solution)
Dissociation of surface groups

• If the particle or droplet has dissociable groups (e.g. -COOH, -NH₂), the ionization gives the substance a net charge

• The dissociation properties and relative proportions of these groups will determine the overall charge
  • When the positive and negative charges cancel each other, the surface is neutral (point of zero charge)

• pH of the solution has a strong effect
  • The pH at which the net charge is zero is called the isoelectric point
Unequal ion dissolution

- Cations are generally more soluble than anions as they have a larger solvate shell

- E.g. for AgI the Ag$^+$ ions are preferentially dissolved and AgI particles in distilled water are negatively charged)

$$\text{AgI} \rightleftharpoons \text{Ag}^+ + \text{I}^-$$

$$K_{\text{AgI}} = a_{\text{Ag}^+} \cdot a_{\text{I}^-} = 7.6 \cdot 10^{-17}$$

$$\Psi_0 = \frac{k_B T}{z e} (\ln a_{\text{Ag}} - \ln a_{\text{Ag}, \text{pzc}}) = \frac{k_B T}{z e} \ln \frac{a_{\text{Ag}}}{a_{\text{Ag}, \text{pzc}}}$$

- $a_{\text{Ag}}$: activity of Ag$^+$
- $a_{\text{Ag}, \text{pzc}}$: activity of Ag$^+$ at zero surface charge
- $k_B$: Boltzmann constant
- $z$: number of posit. charges
- $e$: elementary charge
- $T$: temperature
- $\Psi$: surface potential
Potential-determining ions

- Surface charge of AgI sols

\[ \sigma_0 = F (\Gamma_+ - \Gamma_-) \]

\( \sigma_0 \): surface charge (C/m^2)
\( F \): Faraday constant (C/mol)
\( \Gamma_+ \): surface concentration of cations (mol/m^2)
\( \Gamma_- \): surface concentration of anions (mol/m^2)

- As the solubility product of AgI is very small \( (K = a_{Ag} \cdot a_I = 7.6 \cdot 10^{-17}) \), a slight shift in the balance between cations and anions has a high impact on the surface charge
Potential-determining ions

- At low Ag\(^+\) concentrations, I\(^-\) ions are preferentially adsorbed onto the crystal

- Silver iodide in distilled water has a surface potential of

\[
\Psi_0 = \frac{k_B T}{z F} (\ln a_{Ag} - \ln a_{Ag, pzc}) = 25.7 \text{ mV} \cdot \ln \frac{8.7 \cdot 10^{-9}}{3 \cdot 10^{-6}} = -150 \text{ mV}
\]

- More soluble substances are less influenced by the balance between cations and anions. For AgCl in distilled water, the surface potential is only -20 mV
Potential-determining ions

\[ \Gamma_{Ag^+} = \Gamma_{I^-} \]
\[ \sigma_0 = 0 \]
\[ \text{p.z.c.} \]

\[ \Gamma_{Ag^+} < \Gamma_{I^-} \]
\[ \sigma_0 < 0 \]

\[ \Gamma_{Ag^+} > \Gamma_{I^-} \]
\[ \sigma_0 > 0 \]

AgI in distilled water is negatively charged!

\[ a_{Ag} \approx [Ag^+] \text{ (mol/l)} \]
Effect of pH

- pH of a solution can also have a strong effect on the surface potential of a particle or droplet
- pH influences the dissociation constants of ionizable groups
- Specific adsorption of $\text{H}_3\text{O}^+$ or $\text{OH}^-$ ions

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$\text{pH}_{\text{pec}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz [$\alpha$-SiO$_2$]</td>
<td>2.9</td>
</tr>
<tr>
<td>Amorphous silica [$\text{SiO}_2\cdot\text{2H}_2\text{O}$]</td>
<td>3.5</td>
</tr>
<tr>
<td>Birnessite [$\delta\text{-MnO}_2$]</td>
<td>3.76</td>
</tr>
<tr>
<td>Kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$]</td>
<td>4.7</td>
</tr>
<tr>
<td>Rutile [$\text{TiO}_2$]</td>
<td>5.8</td>
</tr>
<tr>
<td>Anatase [$\text{TiO}_2$]</td>
<td>6.0</td>
</tr>
<tr>
<td>Magnetite [$\text{Fe}_3\text{O}_4$]</td>
<td>6.9</td>
</tr>
<tr>
<td>Muscovite [$\text{KAl}_3\text{Si}_3\text{Al}<em>2\text{O}</em>{10}(\text{OH})_2$]</td>
<td>7.5</td>
</tr>
<tr>
<td>$\gamma$-Alumina [$\gamma\text{-Al}_2\text{O}_3$]</td>
<td>8.5</td>
</tr>
<tr>
<td>Hematite [$\alpha\text{-Fe}_2\text{O}_3$]</td>
<td>8.5</td>
</tr>
<tr>
<td>Gibbsite [$\text{Al(OH)}_3$]</td>
<td>8.9</td>
</tr>
<tr>
<td>Corundum [$\alpha\text{-Al}_2\text{O}_3$]</td>
<td>8.9</td>
</tr>
<tr>
<td>Goethite [$\alpha\text{-FeOOH}$]</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Isomorphous ion replacement

• Many minerals have loosely bound ions
• Exogenous ions can replace these ions while the crystal lattice stays mostly unaffected
• If the valence of the replacing ion is different from that of the original, the particle will have a net charge (E.g. Si\(^{4+}\) to Al\(^{3+}\) substitution in clays → net negative charge)
The Helmholtz model

- Helmholtz, 1850s
- Electrostatic interaction between the surface and counter-ions of the solution
- Electric double layer forms (capacitor)
- Linear potential drop from the surface to the outer Helmholtz plane (OHP)
- Does not take into account
  - thermal motion
  - ion diffusion
  - adsorption onto the surface
  - solvent/surface interactions

\[ \Psi = \Psi_0 \left( 1 - \frac{1}{x_{OHP}} x \right) \]
The Gouy-Chapman model

- Gouy & Chapman, 1909-1913
- Flat, infinite, uniformly charged surface
- Ions considered as point charges
- Boltzmann statistical distribution near the surface
- Accounts for thermal motion
- Counter-ion concentration decreases, co-ion concentration increases from the surface (in the bulk solution the two concentrations become equal)
- Exponential potential decrease
- Debye length \(1/\kappa\): “thickness of the diffuse double layer” or thickness of an equivalent plane capacitor

\[ \Psi = \Psi_0 e^{-\kappa x} \]
The Gouy-Chapman model

Concentration of cations and anions as a distance from the negative surface

Electrostatic potential for different salt concentrations at a fixed surface charge of -0.2 C/m²

κ is proportional to $l^{1/2}$: the double layer thickness decreases with increasing ionic strength

But the model cannot explain charge reversal!
The Stern model

- Stern, 1924
- Combination model: Helmholtz + Gouy-Chapman
- First layer of solvated ions of finite size, tightly adsorbed onto the surface
- Subsequent layers as point charges like in the Gouy-Chapman model
- Slipping (shear) plane: at the boundary of the diffuse layer
- Potential at the shear plane: $\zeta$ or electrokinetic potential
- If shear plane and Stern-plane close enough: $\Psi_{St} \approx \zeta$
- The model can deal with specific ion sorption

$$\Psi = \Psi_0 \left( 1 - \frac{1}{x_{OHP}} x \right)$$

$$\Psi = \Psi_{St} e^{-\kappa(x-x_{OHP})}$$
The Stern model, charge reversal

- If polyvalent or surface-active co-ions are adsorbed, charge reversal can occur.
- In this case, $\Psi_0$ and $\Psi_{St}$ have different sign.
- The elektrokinetic potential ($\zeta$) changes also its sign.
The Stern model, overcharge

- If surfactant co-ions adsorb to the interface, $\Psi_{st}$ can become bigger than $\Psi_0 \rightarrow$ charge increase

- If the Stern plane and the shear planes are close enough, elektrokinetic potential also increase
Electrokinetic phenomena
The shear plane is located close to the outer edge of the Stern layer so Stern potential is close to the zeta potential at low electrolyte concentration.

Electrokinetic potential or zeta potential is the electrostatic potential in the plane of shear.

\[ \psi = \psi_{St} \exp(-\kappa(x - x_{st})) \]

\( x_{st} \) or \( x_{d} \) - distance of Stern plane from the surface.

Positive particle with negative ion atmosphere

The shear plane is located close to the outer edge of the Stern layer so Stern potential is close to the zeta potential at low electrolyte concentration.

\[ \zeta \approx \psi_{St} \]
An electrical double layer exists around each particle.

- The liquid layer surrounding the particle exists as two parts; an inner region (Stern layer) where the ions are strongly bound and an outer (diffuse) region where they are less firmly associated.

Within the slipping plane the particle acts as a single entity.
Electrokinetic phenomena

<table>
<thead>
<tr>
<th>Technique</th>
<th>What Is measured</th>
<th>What Moves</th>
<th>What Causes Movement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrophoresis</td>
<td>Velocity</td>
<td>particles move</td>
<td>applied electric field</td>
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<tr>
<td>Electroosmosis</td>
<td>Velocity</td>
<td>liquid moves in capillary</td>
<td>applied electric field</td>
</tr>
<tr>
<td>Streaming Potential</td>
<td>Potential</td>
<td>liquid moves</td>
<td>pressure gradient</td>
</tr>
<tr>
<td>Sedimentation Potential</td>
<td>Potential</td>
<td>particles move</td>
<td>gravity = gΔρ</td>
</tr>
</tbody>
</table>

1. Electrophoresis
   Particles/molecules move in solution.
2. Electroosmosis
   Liquid moves in capillary.
3. Streaming potential
   The moving liquid generates potential (reverse of electroosmosis).
4. Sedimentation potential
   Moving particles generate potential.
Electrophoretic mobility

\[ F_{el} = QE \]
\[ F_{fric} = f\nu \]

since \( F_{el} = F_{fric} \)

\[ \nu = \frac{QE}{f} \quad \text{mobility} \quad u = \frac{\nu}{E} = \frac{Q}{f} \]
\[ u = \frac{ze}{6\pi\eta r} = \frac{ze}{kT/D} \]

- where \( F_{el} \) the direct electric force, \( E \) is the magnitude of the electric field, and \( Q \) is the particle charge, \( \mu_e \) electrophoretic mobility (V/m), \( \varepsilon \) is the dielectric constant of the dispersion medium, \( \varepsilon_0 \) is the permittivity of vacuum (C² N m⁻²), \( \eta \) is dynamic viscosity of the dispersion medium (Pas), and \( \zeta \) is zeta potential (i.e., the electrokinetic potential of the slipping plane in the double layer) in V.
Electrophoretic mobility

Biochemical proof of protein-DNA interactions using EMSA (electrophoretic mobility shift assay) The method bases on the property that unbound DNA in a non-denatured gel exhibits a higher electrophoretical mobility than protein-bound DNA.

- Gel Electrophoresis
  - Polyacrylamide Gel Electrophoresis (PAGE)
  - Agarose Gel electrophoresis (AGE)

Isoelectric focusing employs a **pH gradient** extending the length of an electrophoresis gel. A protein stops migrating when it enters the zone in which the surrounding pH equals its **isoelectric point, pI**. At any other point in the gradient, the protein acquires a charge which causes it to migrate toward its pI (green and blue arrows).

The stable pH gradient between the electrodes is formed by including a mixture of low molecular weight 'carrier ampholytes' in the inert support. These are synthetic, aliphatic polyaminopolycarboxylic acids available commercially whose individual pI values cover a preselected pH range.

http://www.biochem.arizona.edu/classes/bioc462/462a/NOTES/Protein_Properties/protein_purification.htm
Isoelectric focusing (IEF)

It is important to avoid *molecular sieving* effects so that the protein separation occurs solely on the basis of charge.

The **isoelectric point** is the pH at which the zeta potential is zero. It is usually determined by pH titration: measuring zeta potential as a function of pH. The **point of zero charge** is the pH at which the positive and negative charges of a zwitteric surface are balanced.
Capillary electrophoresis

Diagram: A diagram showing the setup of a capillary electrophoresis system, including a high-voltage power supply, capillary detector, and solvent reservoirs. The diagram also illustrates the charge distribution on the fused silica surface.
Capillary electrophoresis

Motion in capillaries

\[ v_{\text{electroosmotic}} \]

\[ v_{\text{electrophoretic}} \]

\[ v_{\text{total}} = v_{\text{electroosmotic}} + v_{\text{electrophoretic}} \]

Neutral
Schematic illustrating electroosmosis in a capillary. The circles indicate molecules and ions of the indicated charges, as well as their migration speed vector.

Flow profiles in microchannels.

(a) A pressure gradient, $-\nabla P$, along a channel generates a parabolic or Poiseuille flow profile in the channel. The velocity of the flow varies across the entire cross-sectional area of the channel. On the right is an experimental measurement of the distortion of a volume of fluid in a Poiseuille flow. The frames show the state of the volume of fluid 0, 66, and 165 ms after the creation of a fluorescent molecule.

(b) In electroosmotic (EO) flow in a channel, motion is induced by an applied electric field $E$. The flow speed only varies within the so-called Debye screening layer, of thickness $\lambda_D$. On the right is an experimental measurement of the distortion of a volume of fluid in an EO flow. The frames show the state of the fluorescent volume of fluid 0, 66, and 165 ms after the creation of a fluorescent molecule.
Another way to control the EOF (electroosmotic flow) is to modify the wall with coatings.

The capillary wall can be pretreated with a cationic surfactant and the EOF will be reversed, that is, toward the anode.
Streaming potential

\[ U_{\text{sol}} = \frac{C \cdot \varepsilon_i \cdot \varepsilon_0 \cdot \zeta \cdot N}{\eta \cdot \kappa} \cdot V \cdot (\rho - \rho_c) \cdot g \cdot \Delta h \]

Sedimentation potential and Electrodeposition

http://membranes.nist.gov/ACSchapter/toddPAGE.html
http://zeta-potential.sourceforge.net/zeta-potential.shtml
Non-stoichiometric ion adsorption or ion-exchange

The exchange takes place in a "resin bed" made up of tiny bead-like material. The beads, having a negative charge, attract and hold positively charged ions such as sodium, but will exchange them whenever the beads encounter another positively charged ion, such as calcium or magnesium.

Ion-exchange is an equilibrium process:

\[ \text{Resin}-X + Y \rightleftharpoons \text{Resin}-Y + X \]
Non-stoichiometric ion adsorption or ion-exchange

A water softener exchanges the “hardness” causing ions (Ca$^{2+}$, Mg$^{2+}$) to monovalent ions (H$^+$ or Na$^+$)

Ion exchange beds: zeolite, clays, resins.

- When exhausted, ion exchangers need to be regenerated (with the ions to be exchanged for).