Electrical double layer

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http://dragon.unideb.hu/~kolloid/

7. lecture
Adsorption of **strong electrolytes** from aqueous solutions

- Stoichiometric or equivalent
- Non-stoichiometric or ion exchange

Neutral surface

- Ashless charcoal, lyotropic series (Ionic charge and size, Strength of attraction to surface: \( \text{Al}^{3+} > \text{Ca}^{2+} = \text{Mg}^{2+} > \text{K}^+ = \text{NH}_4^+ > \text{Na}^+ \). For anions: \( \text{CNS}^- > (\text{PO}_4^{3-}, \text{CO}_3^{2-}) > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{C}_2\text{H}_3\text{O}_2^- > \text{F}^- > \text{SO}_4^{2-} \))

Non-neutral surface

- Ionic crystal from its solution at a specific concentration

Non-stoichiometric or ion exchange

- Anion-, cation

Electric double layer

?? Which ion goes into the inner layer? (this gives the sign of the surface charge)
Electrical double layer

Surface Charge Density. When a solid emerges in a polar solvent or an electrolyte solution, a surface charge will be developed through one or more of the following mechanisms:

1. **Preferential adsorption** of ions. Specific ion adsorption: Surfactant ions may be specifically adsorbed.

2. **Dissociation of surface charged species** (proteins COOH/COO\(^{-}\), NH\(_2\)/NH\(_3\)\(^{+}\))

3. **Isomorphous replacement**: e.g. in kaolinite, Si\(^{4+}\) is replaced by Al\(^{3+}\) to give negative charges.

4. **Charged crystal surface**: Fracturing crystals can reveal surfaces with differing properties.

http://www.dur.ac.uk/sharon.cooper/lectures/colloids/interfacesweb1.html#_Toc449417608
Electrical double layer

Which is the preferential adsorption of ions?
- The related ions
- The ions which form hardly soluble or dissociable compounds with one of the ions of the lattice
- The ion of larger valences
- $\text{H}^+$ or $\text{OH}^-$

Example: AgCl crystal
AgNO$_3$ or KCl solution
AgCl crystal KBr, or KSCN solution

From NaCl, CaCl$_2$ solution: Ca$^{2+}$

The free acid or base adsorb stronger than the electrolytes, because the mobilities of $\text{H}^+$ and $\text{OH}^-$ are larger.

http://www.dur.ac.uk/sharon.cooper/lectures/colloids/interfacesweb1.html#_Toc449417608
When silver iodide crystals are placed in water, a certain amount of dissolution occurs to establish the equilibrium:

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

The concentrations of Ag\(^+\) and I\(^-\) in solution from the solubility product is very small ($K_{sp} = a_{\text{Ag}^+} \times a_{\text{I}^-} = 10^{-16}$). The slight shifts in the balance between cations and anions can cause a dramatic change in the charge on the surface of the crystals. If there are exactly equal numbers of silver and iodide ions on the surface then it will be “uncharged”.

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

C/m\(^2\) C/mol mol/m\(^2\)
The $\sigma$, C/m² surface charge density changes from positive to negative or vice versa. Zero-charged surface is defined as a point of zero charge (p.z.c.) or zero-point charge (z.p.c.).

$\sigma = \Gamma^- - \Gamma^+$

$\sigma = 0$, p.z.c.

$\sigma > 0$

$\sigma < 0$

The concentration of charge determining ions $\Gamma^+$, mol/m²

$\Gamma^+ < 3 \times 10^{-6}$ mol/l

$\Gamma^+ > 3 \times 10^{-6}$ mol/l

AgI in its own saturated solution is negative!

$c_{Ag^+} = c_I^- = 8.7 \times 10^{-9}$ mol/l

$pAg^{+\text{NTP}} = 5.3$ (AgI)
Potential-determining ions

It seems that the **iodide ions have a higher affinity** for the surface and tend to be preferentially adsorbed. In order to reduce the charge to zero it is found that the silver concentration must be increased by adding a very small amount of silver nitrate solution about to:

\[ c_{\text{Ag}^+} > 3 \times 10^{-6} \text{ mol/l} \]

The charge which is carried by surface determine its electrostatic potential. For this reason they are called **the potential-determining ions**.

We can calculate the surface potential on the crystals of silver iodide by considering the equilibrium between the surface of charged crystal and the ions in the surrounding solution:

\[
\psi_0 = \frac{kT}{Ze} \left( \ln a - \ln a_{\text{PZC}} \right)
\]

Where \( \psi_0 \) the **electrostatic potential difference** (arising form the charge bearers as ions, electrons) **at the interface** \((x=0)\), shortly **surface potential**; \( a \) the activity of the ions and \( a_{\text{PZC}} \) the activity of the ions at **zero-charged surface** in the solution.

\[
\psi_0 = \frac{kT}{Ze} \Delta \ln a \quad \Delta \psi_0 = 25.7 \times \ln \frac{8.7 \times 10^{-9}}{3 \times 10^{-6}} = -150mV
\]

**AgI in its own saturated solution is negatív!**

\( c_{\text{Ag}^+} = c_{\text{I}^-} = 8.7 \times 10^{-9} \text{ mol/l} \)

surface potential of silver iodide crystals placed in clear water
Variable charges surfaces of AgCl crystals

\[ \psi_0 = \frac{kT}{ze} \left( \ln a - \ln a_{PZC} \right) \]

\[ \psi_0 \approx 60 \times (pAg_{pzc} - pAg), mV \]

<table>
<thead>
<tr>
<th>excess [ion]</th>
<th>[Ag], mol/L</th>
<th>pAg</th>
<th>[\psi_0] mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>1.3E-5</td>
<td>4.9</td>
<td>-20</td>
</tr>
<tr>
<td>1x10^{-4} Cl^-</td>
<td>1.8E-6</td>
<td>5.7</td>
<td>-72</td>
</tr>
<tr>
<td>5x10^{-5} Ag^+</td>
<td>5.0E-5</td>
<td>4.3</td>
<td>14</td>
</tr>
<tr>
<td>1x10^{-4} Ag^+</td>
<td>1.0E-4</td>
<td>4.0</td>
<td>32</td>
</tr>
</tbody>
</table>

\[ pAg = -\log_{10}[Ag^+] \]

\[ \ln [Ag^+] = 2.303 \times \log_{10}[Ag^+] \]

\[ pAg^{+}_{NTP} = 4.54 \text{ (AgCl)} \]

\[ K_{spAgCl} = 1.8 \times 10^{-10} \]

surface potential of silver chloride crystals placed in clear water (its own saturated solution) is \( \sim -20 \text{ mV} \)
Surface charges in oxides, pzc

\[ \psi_0 = \frac{kT}{ze} 2.303(pH_{pz} - pH) \approx 60 mV \times \Delta pH \]

The surface charge in oxides is mainly derived from preferential dissolution or deposition of ions. Ions adsorbed on the solid surface determine the surface charge, and thus are referred to as charge determining ions, also known as co-ions or coions. In the oxide systems, typical charge determining ions are protons and hydroxyl groups and their concentrations are described by pH (\(= - \log_{10} [H^+]\)).

As the concentration of charge determining ions varies, the surface charge density changes from positive to negative or vice versa. The concentration of charge determining ions corresponding to a neutral or zero-charged surface is defined as a point of zero charge (p.z.c.) or zero-point charge (z.p.c.).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>pH_{pz}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz [(\alpha)-SiO_2]</td>
<td>2.9</td>
</tr>
<tr>
<td>Amorphous silica [SiO_2\cdot2H_2O]</td>
<td>3.5</td>
</tr>
<tr>
<td>Birnessite [(\delta)-MnO_2]</td>
<td>3.76</td>
</tr>
<tr>
<td>Kaolinite [Al_2Si_2O_5(OH)_4]</td>
<td>4.7</td>
</tr>
<tr>
<td>Rutile [TiO_2]</td>
<td>5.8</td>
</tr>
<tr>
<td>Anatase [TiO_2]</td>
<td>6.0</td>
</tr>
<tr>
<td>Magnetite [Fe_3O_4]</td>
<td>6.9</td>
</tr>
<tr>
<td>Muscovite [KAl_2(Si_2Al)O_10(OH)_2]</td>
<td>7.5</td>
</tr>
<tr>
<td>(\gamma)-Alumina [(\gamma)-Al_2O_3]</td>
<td>8.5</td>
</tr>
<tr>
<td>Hematite [(\alpha)-Fe_2O_3]</td>
<td>8.5</td>
</tr>
<tr>
<td>Gibbsite [Al(OH)_3]</td>
<td>8.9</td>
</tr>
<tr>
<td>Corundum [(\alpha)-Al_2O_3]</td>
<td>8.9</td>
</tr>
<tr>
<td>Goethite [(\alpha)-FeOOH]</td>
<td>9.0</td>
</tr>
</tbody>
</table>
The structure of the electrical double layer. The diffuse double layer

The electric double layer consists of two regions: an inner region including adsorbed ions and a diffuse region in which ions are distributed according to the influence of electric forces and random thermal motion. The simplest quantitative treatment the diffuse part of DL is assumed (Gouy and Chapman model)
1. surface is flat, infinite, uniformly charged.
2. the ions are point charges distributed according to the Boltzmann distribution.

The electric potential \( \psi_0 \) at a flat surface and \( \psi \) at distance \( x \) from the surface in the electrolyte solution. The potential decreases exponentially with distance from the charged surface:

\[
\psi = \psi_0 \exp(-\kappa x)
\]

\( \kappa \) Debye-Hückel parameter

The ions would be moving about as a result of their thermal energy.
The structure of the electrical double layer

Gouy-Chapman model

\[ \psi = \psi_0 \exp\left(-\kappa x\right) \]

**Surface potential**

1/\(\kappa\) the thickness of the DL;
\(\kappa \sim I^{1/2}\) ionic strength

\[ \kappa = \left(\frac{e^2 \sum \chi_i^0 \epsilon_i^2}{\varepsilon_0 \varepsilon_r \kappa_B T}\right)^{1/2} \]

Diffuse layer of counter ions as a result of their thermal energy and electric forces.
Boltzmann distribution of ions near the charged surface

\[ n_+ = n_\infty e^{-ze\psi/kT} \quad n_- = n_\infty e^{+ze\psi/kT} \]

The concentration of ions as a distance of negative surface

Electrical potential

\[ \kappa = \left( \frac{e^2 \sum z_i^2}{\varepsilon \varepsilon_0 \kappa_B T} \right)^{1/2} \]

Electrolyte concentration increases from curves (1) to (3)

Distance from colloidal particle

The potential distribution near the surface at different values of the (indifferent) electrolyte concentration for a simple Gouy-Chapman model of the double layer. \( c_3 > c_2 > c_1 \). For low potential surfaces, the potential falls to \( \psi_0/e \) at distance \( 1/\kappa \) from surface.

It couldn’t explain the charge reversal.
In the Stern model in the outer layer there is a **compact region close to the surface containing an excess of one type of ion**. A region called the diffuse layer where the Gouy-Chapman treatment still applies.

**Figure 2.14**

**Stern model**

In the Stern model in the outer layer there is a **compact region close to the surface containing an excess of one type of ion**. A region called the diffuse layer where the Gouy-Chapman treatment still applies.
Stern model

Finite ion size, specific ion sorption, compact layer

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

\( \kappa \): a Debye Hückel parameter

1/ \( \kappa \) the thickness of DL

\[
\begin{align*}
n_+ &= n_\infty \frac{e^{-z_+\psi}}{kT} \\
n_- &= n_\infty \frac{e^{+z_-\psi}}{kT}
\end{align*}
\]

the electrostatic interactions are in competition with Brownian motion in the diffuse layer (G-Ch treatment)

The whole DL is electrically neutral.
Stern model, charge reversal

\[ \Phi / V \]

\[ \psi \]

\[ \psi_{0} \] face potential

\[ \Phi_{d} \] Stern-p.

\[ \psi_{St} \] potential

\[ x \] (indiv.u.)

Electrostatic term depends on z

\[ \zeta \]

chemical term \( \geq 0 \)

\[ \Theta = \frac{K_n}{1 + K_n} \]

\[ K \approx \exp \left( \frac{ze\psi_{s} + \phi}{kT} \right) \]
Stern model, charge increase

\[ K \approx \exp\left( \frac{z\psi_s + \phi}{kT} \right) \]