Colloid Chemistry

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Diffuse double layer: extension to Gouy-Chapman model

Theoretical inconsistency of Poisson-Boltzmann equation waived in the limit of small potentials (DH approximation: $z_i \cdot e \cdot \psi << k_B T$)

$$\Psi(x) \cong \Psi_0 \exp(-\kappa x)$$

Poisson-Boltzmann without limitations of DH approximation → development of **Gouy-Chapman theory for EDL**: derivation of an equation describing variation in potential with distance from the surface for diffuse double layer without the simplifying DH approximation of low potential:

$$\Upsilon = \Upsilon_0 \exp(-\kappa x)$$

$$\Upsilon = \frac{\exp(ze\psi/2k_B T)-1}{\exp(ze\psi/2k_B T) + 1}$$

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Diffuse double layer: extension to Gouy-Chapman model

\[ \Psi(x) \approx \Psi_0 \exp(-\kappa x) \]

(\textit{note: } \Psi = \left[ \exp\left(\frac{z e \psi}{2 k_B T}\right) - 1 \right] / \left[ \exp\left(\frac{z e \psi}{2 k_B T}\right) + 1 \right])

\[ \Psi = (4k_B T / ze) \Psi_0 \exp(-\kappa x) \]

for very large values of \( x \)

for very large values of \( \Psi_0 \Rightarrow \Psi_0 \rightarrow 1 \)

potential in the outer portion of diffuse double layer is \textit{independent} on the potential on the surface

for \textit{low potential} becomes

\[ \exp\left(\frac{z e \psi}{2 k_B T}\right) = 1 + \frac{z e \psi}{2 k_B T} \]
\[ (e^x = 1 + x + x^2/2! + x^3/3! \ldots) \]

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Inert and potential determining ions

**potential-determining (p.d.) ions**
Species which by virtue of their electron distribution between the solid and liquid phase (or by their equilibrium with electrons in the solid) determine the difference in potential between these phases. This definition requires that adsorbed p.d. ions are part of the adsorbent and belong to the category of surface ions (http://goldbook.iupac.org/P04776.html)

Es: Ag⁺ and I⁻ ions in AgI sols, H⁺ in oxides (potential pH-determined)

**inert (indifferent) ions**
They do not change the charge density at the surface of the particles, but may influence the interfacial potential difference by virtue of their local distribution (e.g. NaNO₃)
specifically adsorbed ions

inner Helmholtz plane (IHP)
The locus of the electrical centres of specifically adsorbed ions.

outer Helmholtz plane (OHP)
At an electrified interface, the locus of the electrical centres of non-specifically adsorbed ions in their position of closest approach.

IUPAC Goldbook
Some ions (favourable interactions with surface) may lose some of the molecule in the solvation shell and move close to the IHP.

**specific adsorption**
Ions become specifically adsorbed when short-range interactions between them and the **interphase** become important. They are believed then to penetrate *into the inner layer* and may (but not necessarily) come into contact with the surface. They are usually assumed to form a partial or complete **monolayer**. **Determine the value of \( \psi_0 \).**

**non-specific adsorption**
Ions approach an **interface** differently depending on the forces in play. Ions are non-specifically adsorbed (positively or negatively) when they are subjected in the **interphase** only to **long-range coulombic interactions** (attraction or repulsion). They are believed to retain their **solvation** shell, and in the position of closest approach to the **interface** they are separated from it by one or more molecular layers.
specifically adsorbed ions

In the **Stern layer** (ions absorbed on the charged surface):

→ Inner Helmoltz Plane):

- Dielectric constant of water lower than in the bulk (dielectric saturation*) due to very high local electric field in this region
- Charge are not point charges but volume should be considered
- Strength of specific adsorption at the interface is different depending on the nature of the ions
- Surface saturation limit can be approached
- **Colloidal stability affected by the outer region, not by Stern layer**


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strength of specific adsorption

I⁻ > SCN⁻ > Br⁻ > Cl⁻ > OH⁻ > F⁻

N(C₂H₅)₄⁺ > N(CH₃)₅⁺ > Tl⁺ > Cs⁺ > Na⁺

Specific adsorption enhanced by
1. larger size (= larger polarizability) and
2. lower hydration
specifically adsorbed ions

screening effect of the ions gradually reduces the zeta potential (not the surface potential), and this asymptotes to zero at high electrolyte concentrations.

As concentration of specifically adsorbed ions is increased, they also screen the zeta potential, but the additional chemical (as distinct from electrostatic) binding on the surface causes sufficient adsorption of ions for the original particle charge to be neutralised and then reversed as the electrolyte concentration increases. In such a system we see a point of zero charge or PZC at a well defined electrolyte concentration, prior to charge reversal.
When two colloids interact

**overlap of the electrical double layers in lyophobic colloids**

difference in bulk local ion concentration with respect to that in the midpoint:

- **osmotic pressure** → *force the particles apart*

Integration of *force* with respect to the distance gives *energy*

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When two colloids interact

A simpler result can be obtained for the interaction between diffuse electrical double layers, if we assume we are dealing with only low electrostatic potentials (Debye-Hückel approximation).

\[ \Psi(x) \ll 25 \text{ mV} \]

Further assumption: two planar surfaces.

\[ \Psi(x) = \Psi_0 \exp(-\kappa x) \]
When two colloids interact

Recall that the Debye length is:

\[
\kappa^{-1} = \left[ \frac{\varepsilon \varepsilon_r kT}{e^2 \sum_i z_i^2 n_i} \right]^{1/2}
\]

\[
\kappa = \left[ \frac{1000e^2 N_A \sum_i z_i^2 M_i}{\varepsilon_0 \varepsilon_r k_B T} \right]^{1/2}
\]
When two colloids interact (in electrolyte)

Non-interacting surfaces

$x \gg \kappa^{-1}$

Interacting Surfaces

$x < \kappa^{-1}$

For interacting surfaces we apply the superposition approximation*, which means the total potential at point $x$ is given by the sum of the unperturbed potential from each surface.

*admissible when surfaces are sufficiently apart so that the overlap of EDL is moderate

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When two colloids interact

recall that:\[ \Psi(x) = \Psi_o \exp(-\kappa x) \]
potential at the midplane m corresponding to x/2:

\[ \Psi(m) = 2\Psi_o \exp(-\kappa \frac{x}{2}) \] (2)

At the midpoint (m) the gradient of the potential is zero
\[ \frac{d\Psi(x)}{dx} = 0 \] (minimum):

Therefore **no net electric field** is acting on the ions at this point.

at the midpoint there is a **higher total concentration of ions** than in the bulk → **osmotic pressure** will then act to dilute the ions by drawing water into the region between the interacting surfaces.

→ **electrical double-layer repulsion** between the charged plates
→ from osmotic pressure at the mid-plane: repulsive pressure between the surfaces.
When two colloids interact

The osmotic pressure $\Pi$ of an ideal solution is given by

$$\Pi = cRT$$  \hspace{1cm} (3)

where, $c$ is the solute concentration.

**Repulsive pressure ($\Pi_R$):** difference between osmotic pressure at the mid-plane and the bulk solution:

$$\Pi_R = RT \sum_i (c_i^m - c_i^{bulk})$$  \hspace{1cm} (4)

where $i$ refers to each ionic solute $c_i^m$ and $c_i^{bulk}$ are the concentrations of each ionic solute in the mid-plane (m) and in bulk solution, respectively.
When two colloids interact

mid-plane potential varies with surface separation (equation 2): use the Boltzmann equation to calculate the concentrations of each ion at the mid-plane. By this procedure, assuming low potentials we obtain the result:

\[
\Pi_R = \frac{1}{2\varepsilon_0\varepsilon_r} \kappa^2 \Psi_0^2 \exp\left(-\kappa x\right)
\]  \hspace{1cm} (5)

where the double-layer repulsive energy (related to pressure) decays exponentially with distance and depends on

I. the Debye length (i.e. electrolyte concentration)
II. the surface potential
III. the type of electrolytes
Interactions between overlapping EDL:

- magnitude of the surface potential
- thickness of the EDL
- type and concentration of electrolytes
- type of surface equilibrium conditions existing prior to interaction

**Two limiting cases when particles come together:**

1. If surface charge results from adsorption of p.d.i., **surface potential remains constant** as the two surface approaches (adjustment of charge densities) (CONSTANT POTENTIAL)
2. If surface charge is deriving from surface ionisation: **surface charge remains constant, potential readjusts** (CONSTANT CHARGE)

Difference between 1. and 2. not relevant for big distances
Expression can be derived for calculation of interactions for both constant charge and potential in the interaction of not identical spheres (surface potential may be different) (cfr: heterocoagulation)
Interactions between overlapping EDL

If surface charge result of adsorption of p.d.i., **surface potential remains constant** as the two surface approaches (**adjustment of charge densities**) (**CONSTANT POTENTIAL**)

\[
V_R^\Psi = \frac{1}{2} \varepsilon a \Psi_0^2 \ln[1 + e^{x}(\!-\! \kappa H)]
\]

If surface charge is deriving from surface ionisation: **surface charge remains constant**, **potential readjusts** (**CONSTANT CHARGE**)

\[
V_R^\sigma = \frac{1}{2} \varepsilon a \Psi_0^2 \ln[1 - e^{x}(\!-\! \kappa H)]
\]

H = distance of closest approach between particles
r = centre-to-centre distance
a = radius of the particles

Addition of **charged colloidal particles** to a solution  
Assumption: background electrolyte concentration is low/concentration of particle added high.

- add counter-ions with each particle
- reduce the solution volume available to ions

\[
\kappa^2 = \left[ \frac{e^2 \sum_i z_i^2 n_i \infty}{\varepsilon_0 \varepsilon_r k_B T} \right] \rightarrow \kappa^2 = \left[ \frac{e^2 z^2}{\varepsilon_0 \varepsilon_r k_B T} \cdot \frac{2n_0 + \frac{3\sigma \Phi}{ae}}{1 - \Phi} \right]  
\]

\[ z = \text{counter-ion valency} \]
\[ n_0 = \text{concentration of the counter-ion (added electrolyte)} \]
\[ a = \text{particle radius} \]
\[ e = \text{formal charge of electrons} \]
\[ \Phi = \text{volume fraction of particles} \]

Relevant if:
- particles are small
- **volume fraction** \( \Phi \) and surface charge are high

Takes into account the counter-ions which are carried by the particle through the surface charge density \( \sigma \)
Effect of different background electrolytes as a function of particles volume fraction

Conditions:
Radius 85 nm
Surface charge density: 0.15 μCcm\(^{-2}\)

\[
\kappa^2 = \left[ \frac{e^2 z^2}{\varepsilon_0 \varepsilon_r k_B T} \right] 2n_0 + \frac{3\sigma\Phi}{ae} \cdot \frac{2n_0 + \frac{3\sigma\Phi}{ae}}{1 - \Phi}
\]
When two colloids interact: electrostatic repulsion

**Electrostatic repulsion** important stabilising mechanism for particles in polar solvents

Diffuse part of EDL exends in solution over $\kappa^{-1}$ ($\kappa^{-1}$ rate of decay of the potential in the EDL):

$\rightarrow \kappa^{-1}$ defines the extent to which the ionic atmosphere (different from the bulk ionic medium) extends from particle surface