(7) SOLID-LIQUID INTERFACES

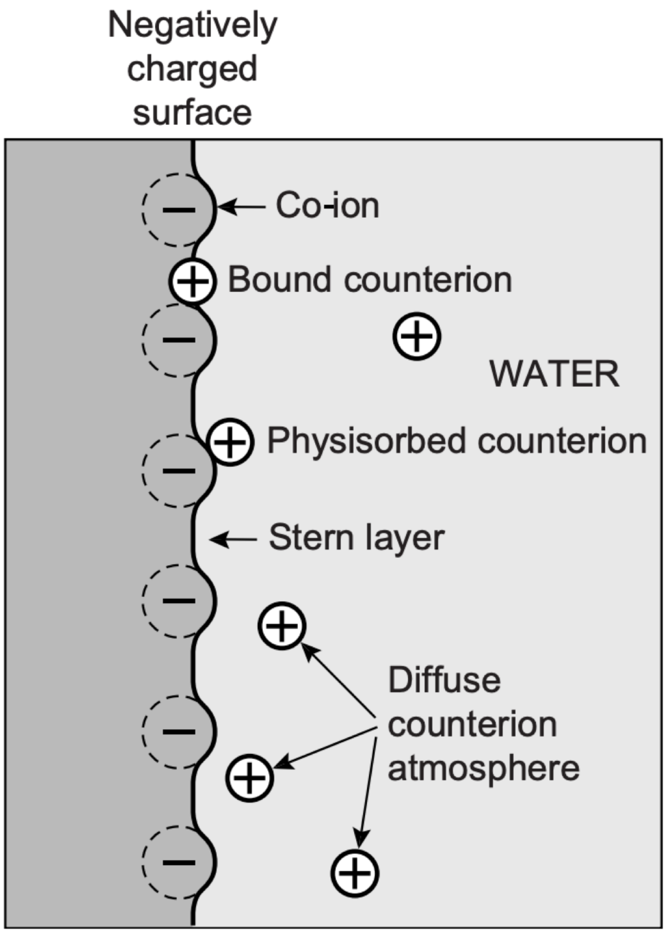
DISTRIBUTION OF CHARGE, CONDUCTION PROPERTIES, ELECTRICAL PROPERTIES

Intermolecular and surface forces. J. Israelashvili
Chapter 14

Solid Surfaces in a Liquid

what happens when the two surfaces are in contact to each others: counterions that can bind, physisorb or keep moving thanks to brown motions

Pure Water*



Stern layer: ions are not rigidly bound but can exchange with other ions in solution; their lifetime on a surface can be as short as 10^{-9} s or as long as many hours.

layer that contains bound counterions.

*contains a 10^{-7} M of ionized water molecules (H_3O^+ OH^-)

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Calculating the density of counterions at the surface

$$\rho_s = \frac{\sigma^2}{2\varepsilon_0 \epsilon_r KT}$$ concentration of counterions at the surface

volumetric concentration that only depends on surface charge

ro(s)c : counterions that the surface attract to respond to the surface charge

Where, $\sigma = -0.2\ C/\mathrm{m}^2$ is the Surface charge (intrinsic surface charge and co-ions)

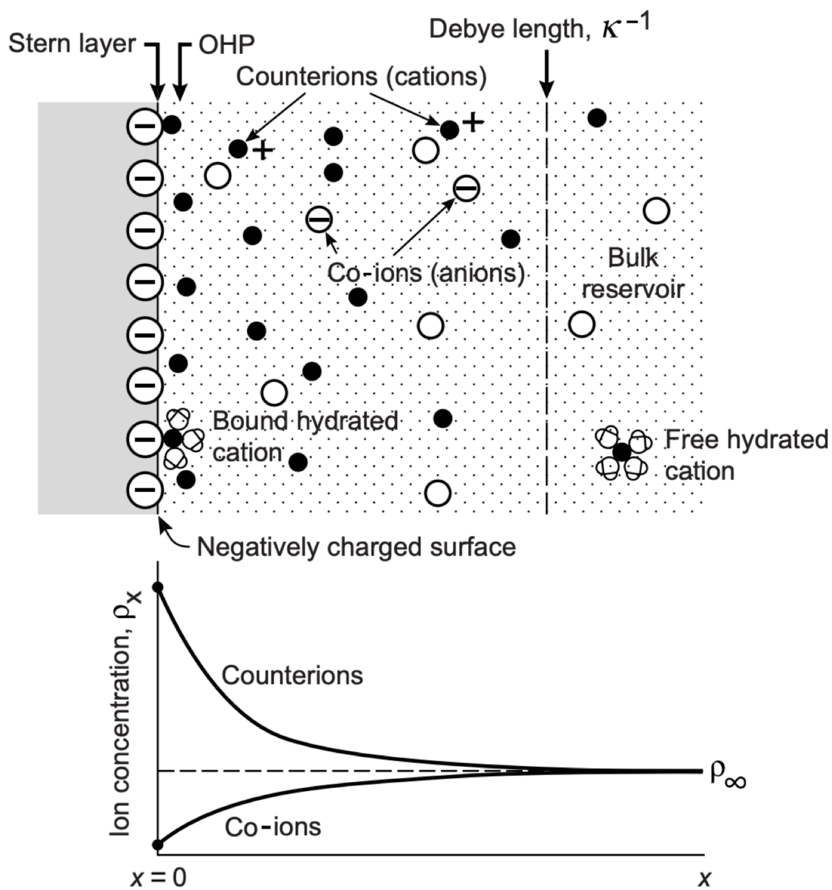
Knowing that the Thickness of counterions charged layer is around 0.2 nm, we can calculate the

Density of counterions : σ_s 1.4 10^{18} ions/m^2

Given the Elementary charge : 1.6 10^{-19} C,
The charge of σ_s is 0.2 C/m^2 , fully compensating σ in this case (i.e. for an highly charged surface)

Solid Surfaces in a Liquid

Presence of an electrolyte*



Near the surface:

- Excess of counterions from the electrolyte
- Depletion of co-ions from the electrolyte
- Counterions can adsorb to the surface in the dehydrated, partially hydrated, or fully hydrated state

*Electrolyte concentration in animal fluids: 0.2M. In the sea: 0.6M

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Surface potential and Surface charge σ

Variation of Surface Potential with Aqueous Electrolyte Concentration

Surface of Charge Density σ = - 0.2 C/m²

1:1 Electrolyte Concentration (M)	ψ_0 (mV) Pure 1:1 Electrolyte Solution
0 (hypothetical)	$-\infty$
10^{-7} (pure water)	−477
10^{-4}	−300
10^{-3}	−241
10^{-2}	−181
10^{-1}	−123
1	−67

Grahame equation with NaCl

$$\sigma_0 = \sqrt{8\varepsilon_r\varepsilon_0\, k_B T\, c_0}\,\sinh\left(\frac{q\Psi_0}{2\,k_B T}\right)$$

Grahame equation with NaCl and $CaCl_2$

$$\begin{aligned}\sigma &= \sqrt{8\varepsilon_0\varepsilon kT}\sinh(e\psi_0/2kT)\{[\mathrm{Na}^+]_\infty + [\mathrm{Ca}^{2+}]_\infty(2+e^{-e\psi_0/kT})\}^{1/2}\\ &= 0.117\sinh(\psi_0/51.4)\{[\mathrm{NaCl}] + [\mathrm{CaCl_2}]_\infty(2+e^{-\psi_0/25.7})\}^{1/2}\ \ \mathrm{C\,m^{-2}}\end{aligned}$$

Calculating the surface charge

Grahame equation with NaCl and $CaCl_2$

$$\begin{aligned}\sigma &= \sqrt{8\varepsilon_0 \varepsilon kT}\sinh(e\psi_0/2kT)\{[\mathrm{Na^+}]_\infty + [\mathrm{Ca^{2+}}]_\infty(2+e^{-e\psi_0/kT})\}^{1/2} \\ &= 0.117\sinh(\psi_0/51.4)\{[\mathrm{NaCl}] + [\mathrm{CaCl_2}]_\infty(2+e^{-\psi_0/25.7})\}^{1/2}\ \mathrm{C\,m^{-2}}\end{aligned}$$

e.g.:

- If the Potential in physiological saline solution (150mM NaCl) is -75 mV ,
- the surface charge density equals

  to 0.117 $(0.150)^{1/2}$ sinh(-75.0/51.4) = - 0.0922 C m^{-2} .

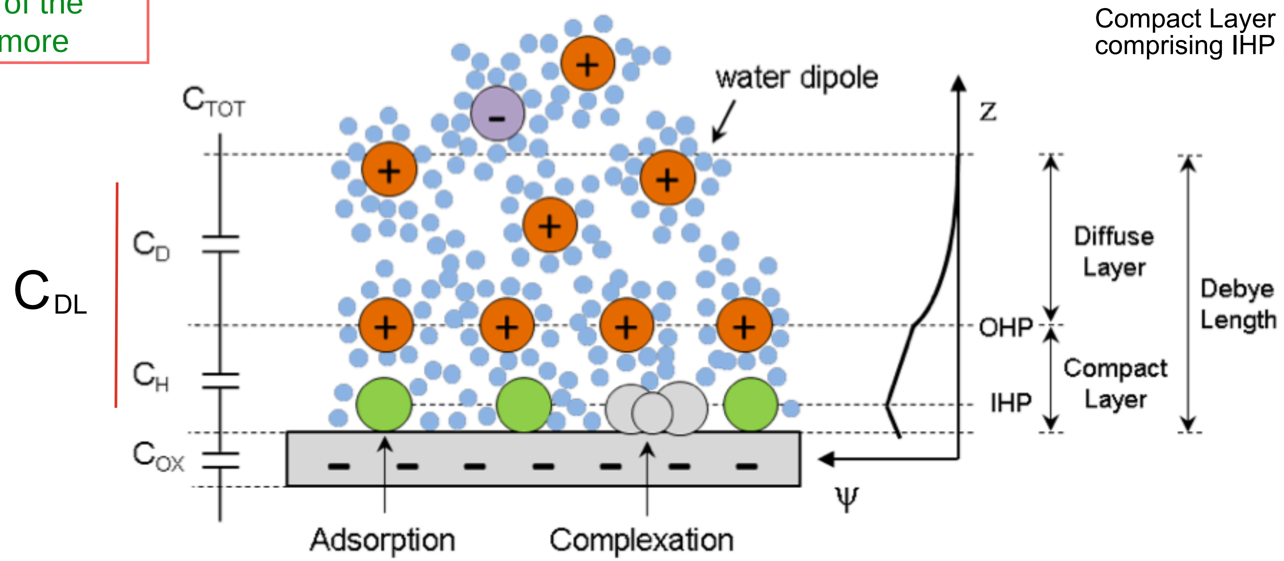
The capacitance model at the interface

how can we relate this picture to an electrical model? next slides

after debye lenght we can say that we can't see the influence of the layer anymore

Diffuse Layer = Gouy-Chapman layer

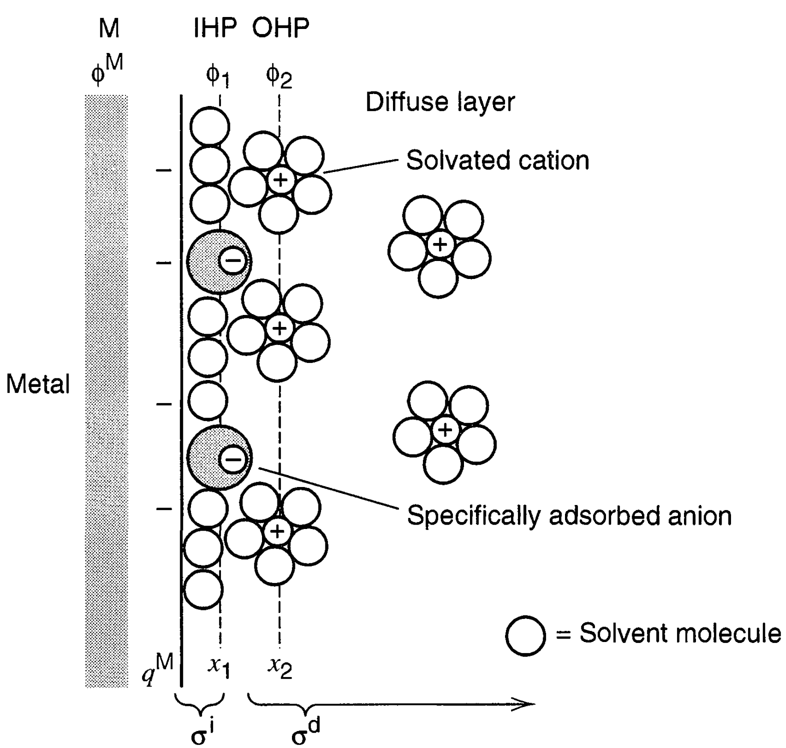
Compact Layer = Stern Layer, comprising IHP and OHP



When immersing a solid material in an aqueous solution, a surface charge forms at the solid surface due to differences in their electrochemical potentials. This surface charge consists of an excess or deficiency of electrons that attracts counter ions from the electrolyte. The net charge of the counter ions is equal and opposite of the net surface charge, so as to assure the electrical neutrality of the system. On the other hand, the counter ions charge attracts also aggregates of water molecules, which are dipoles with an asymmetric charge distribution. Under no external energy source, the charges in the electrolyte will be symmetrically distributed to minimize the total energy of the system.

Electrical Double layer (Metal). – Electrified interface 1879

METAL



Stern layer: first molecular layer. water molecules and Specifically Adsorbed Ions (non necessarily counterions)

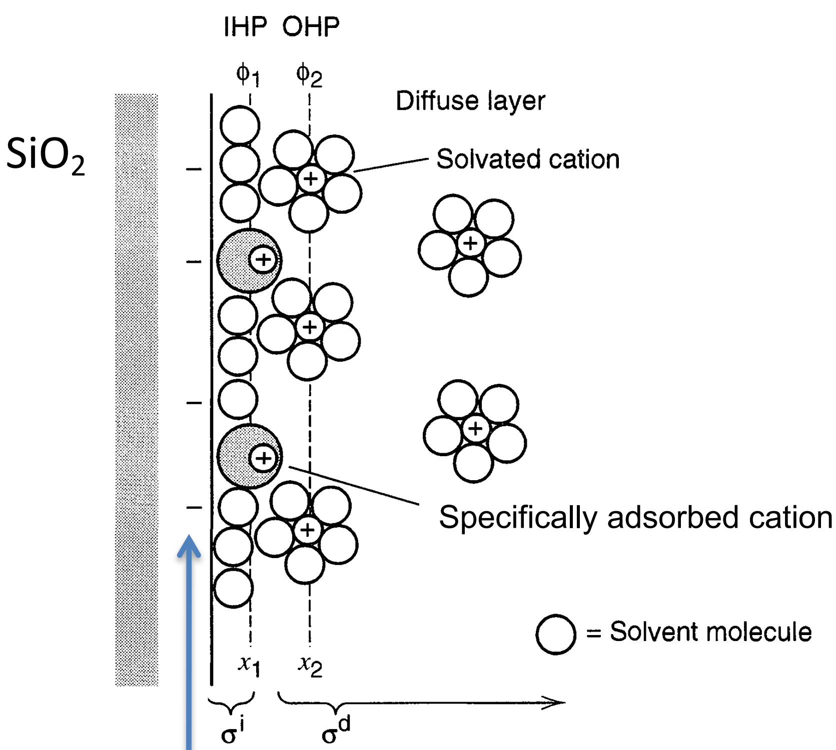
IHP: inner Helmholtz plane: locus of the electrical center of the Specifically Adsorbed Ions

Diffuse layer: counterions surrounded by water molecules. Thickness of the diffuse layer: less than 100 Å for 10^{-2} M electrolyte.

OHP: outer Helmholtz plane: locus of the electrical center of the Non Specifically Adsorbed Ion

Electrical Double layer (Insulator)

INSULATOR (silica)



Deprotonated Silanol groups (SiO^-)

Stern layer: first molecular layer. water molecules and Specifically Adsorbed Ions (non necessarily counterions)

IHP: inner Helmholtz plane: locus of the electrical center of the Specifically Adsorbed Ions

Diffuse layer: counterions surrounded by water molecules. Thickness of the diffuse layer: less than 100 Å for 10^{-2} M electrolyte.

OHP: outer Helmholtz plane: locus of the electrical center of the Non Specifically Adsorbed Ions

Electrical double layer

The counter ions which compensate for the net surface charge form an electrical double layer (EDL), which can be spatially divided in different sections.

GOUY-CHAPMAN LAYER: The layer closest to the bulk solution is called the diffuse layer (or Gouy-Chapman layer) . Within this layer, ions are not fixed, but they tend to diffuse, creating an electrostatic potential in the electrolyte that can be described by combining the Poisson equation with the Boltzmann statistic.

STERN LAYER The diffuse layer is followed by the compact layer which is formed by counter-ions in direct vicinity to the solid-electrolyte interface, at a distance known as the outer Helmholtz plane (OHP) (Non-specific adsorption: the ions retain their solvation shell, but are adsorbed onto the surface by distant Coulombic attractions). In addition to the distribution of the counter-ions, adsorption of ions on the surface also influences the potential of the double layer. Typically, these are the ions that get rid of the water aggregates and, therefore, can approach the surface much more, at a distance known as the inner Helmholtz plane (IHP) (Specific adsorption) .

Electron transfer at Electrolyte/electrode interfaces

- Electron-transfer reaction can occur and lead to a potential difference across the solid-electrolyte boundary.
  - For instance, due to an initial transient charge exchange between the two conductors
  - Movement of the electrons is a kind of “hopping” and is the result of reduction and oxidation of dissolved species in solution.
  - At equilibrium, electrons cross the electrified interface in both directions. Oxidation and reduction continue to occur at the same rate in presence of an equilibrium potential difference.

Electrolyte/electrode interfaces

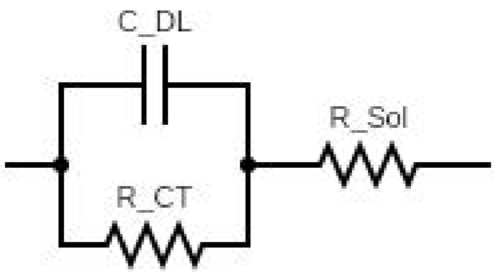
- In case an overpotential is added, the current has the form of the Butler-Volmer equation:

$$I = I_0\left[e^{(1-\beta)\eta zq/kT} - e^{-\beta\eta zq/kT}\right]$$

where η is the overpotential, β is the symmetry factor 0< β<1, zq the charge of the species

Electrolyte/electrode interfaces

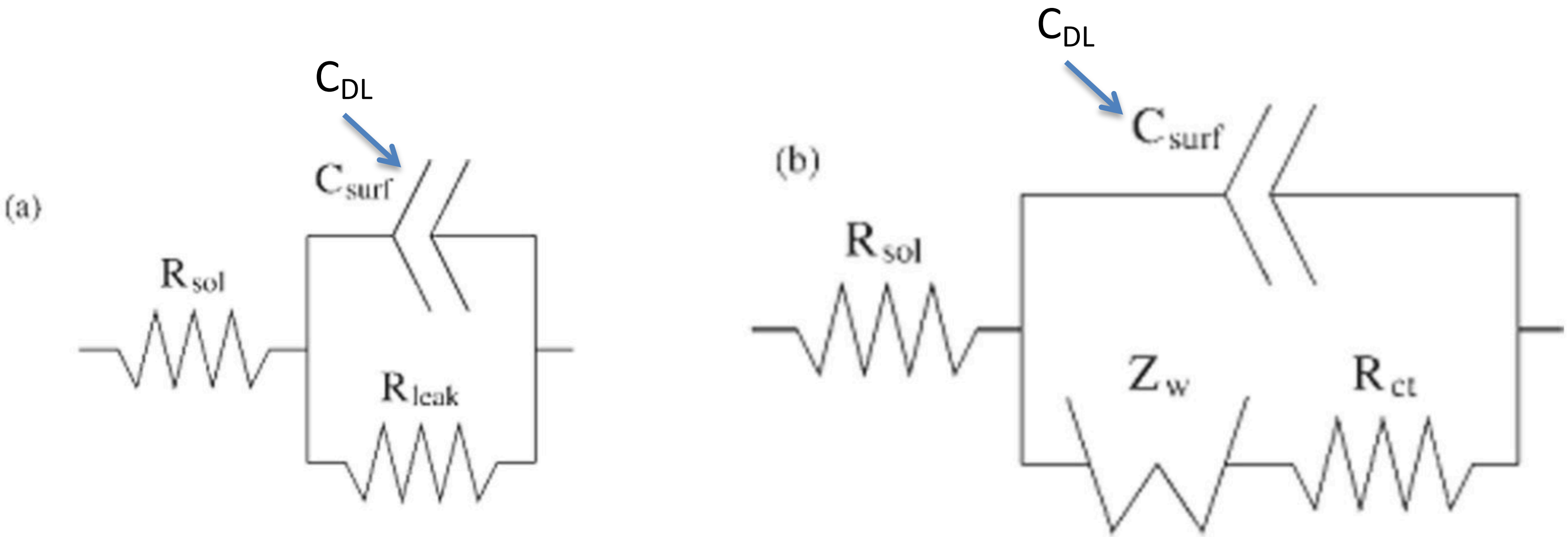
Electrical model of the interface (1st approximation)



- Ideally nonpolarizable interface
  - Potential difference is fixed. R_{CT} -> 0.
    - Such electrodes are called "reference electrodes" or non polarizable interfaces.
  - The potential difference changes as a consequence of any variation of the potential difference across the whole system which includes the interface. R_{CT} -> ∞
    - Called Ideally polarizable interfaces or blocking interface
- Equivalent circuit with R_{CT} and C_{DL}

  The charge transfer resistance is included in the model only if Faradaic processes are non negligible

Electrical model of the interface



Non faradaic processes

Minor charge transfer effects

Faradaic processes (resulting in a non negligible net current through the interface)

- Charge transfer due to oxidation/reduction reactions at the interface
- Charge transfer resistance (R_{CT}) due to:
  - Overpotential
  - energy barrier of the redox species reaching the electrode

Z_w Warburg impedance, small for high frequencies, large for low frequencies. It is caused by diffusion of species