The Electrolyte Double-Layer and Electrokinetic Effects p114

When an electron conductor is brought in to contact with a solid or liquid an excess of charge forms at the surface.

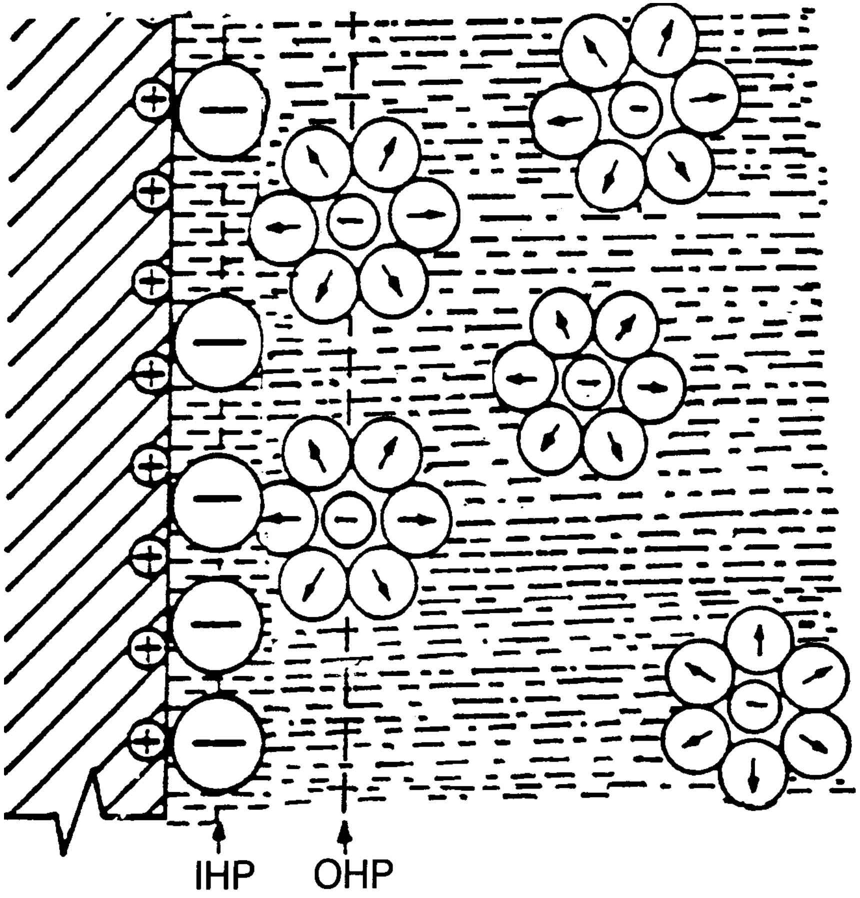
This is the main reason for the formation of *the electrical double layer* at the interface of two phases.

Example:
A metal, M, is brought into contact with a solution of its ions, M^{z+},

$$M^{z+} + ze^{-} \Leftrightarrow M$$

If the reduction reaction dominates, this will cause excess of ⊕ at the metal surface and ⊖ will be attracted from the solution thus forming a charged electrical double layer so the metal and solution have a different potential, φ.

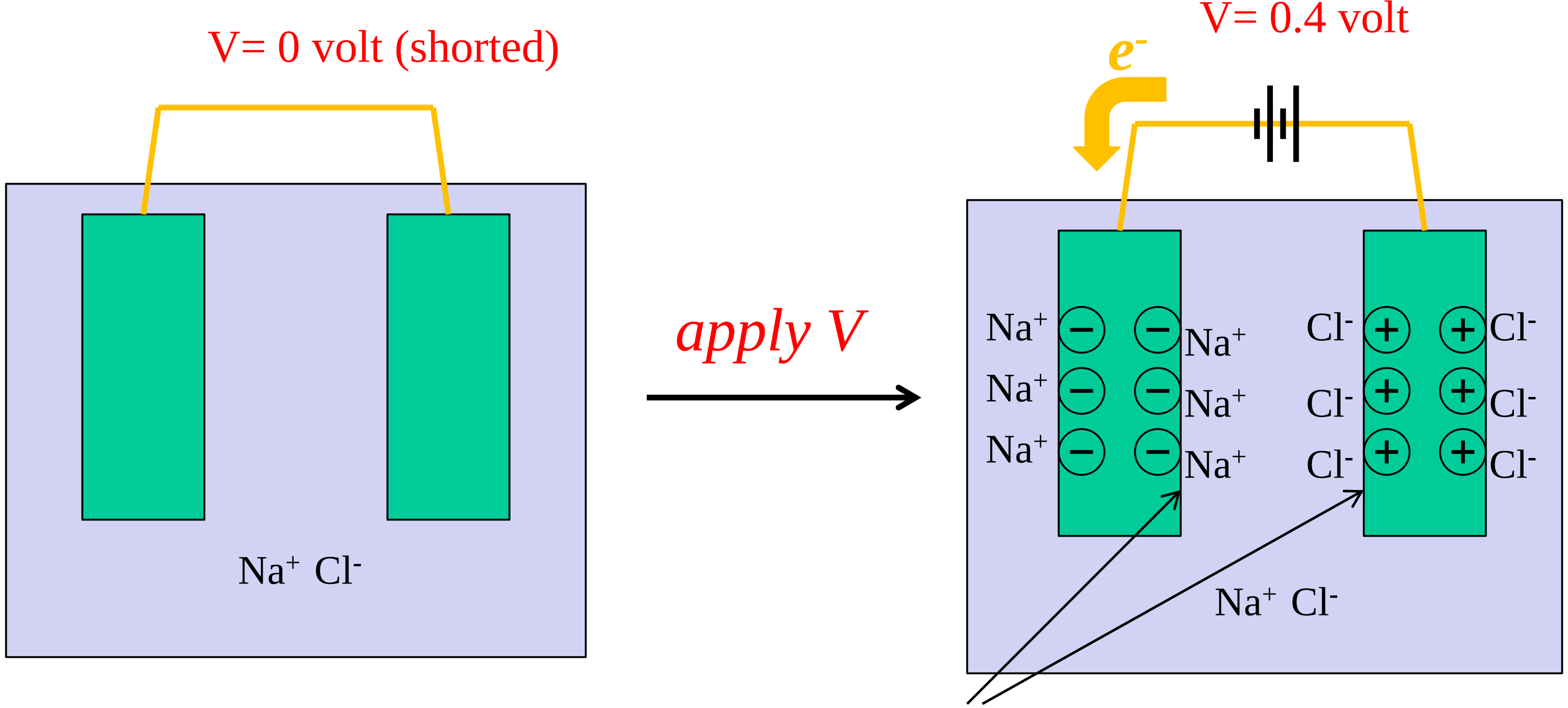
$$\varphi_M \neq \varphi_S$$



Schematic representation of the *electrical double layer*

Ideally Polarizable Electrode

The equilibrium potential at an *ideally polarizable electrode**can be disturbed by applying an *emf* (V) between that electrode and another (counter) electrode in the same solution.



This results in the formation of an *electric double layer* at each electrode surface.

What does this metal surface look like at the atomic level?

***Note: definition of "ideally polarizable electrode":**

An ideally polarizable electrode experiences no Faradaic reactions (no electron transfers between electrode and chemicals in solution) over a specified range of electrode potentials.

What does this metal surface look like at the atomic level?

Helmholtz and Diffuse Double Layer Model

Helmholtz double layer model

The ions approach the surface of the electrode as closely as possible.
The double layer then consists of two parallel layers of charge,

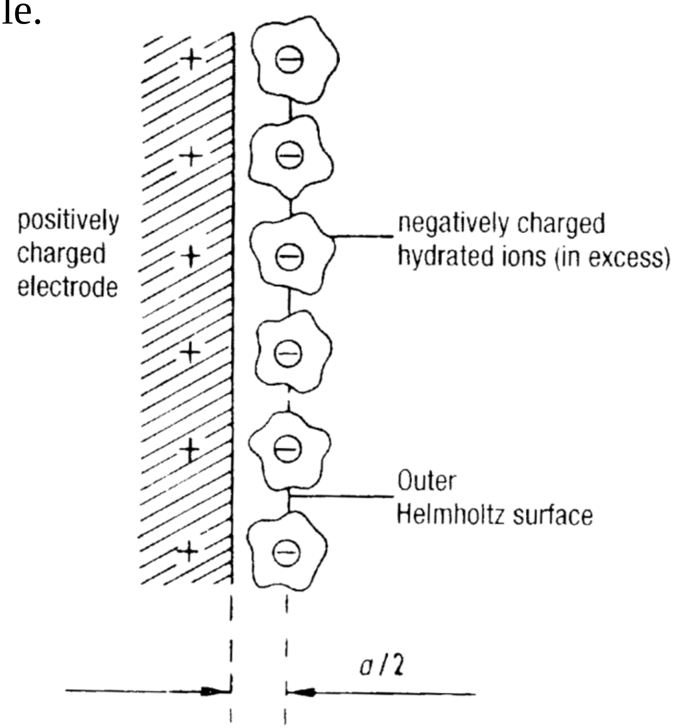
- one on the metal surface and
- one comprising ions at the distance of closest approach.

Consequence:
This way the double layer will be best described by a capacitor with a plate separation ***a / 2*** where ***a*** is the diameter of the ion (possibly solvated).

Math Description:
The connection between the space charge density and the potential is given by the Poisson equation:

$$\frac{d^2\varphi}{dx^2} = -\frac{\rho}{\varepsilon_r \varepsilon_0}$$

Where *x* is the direction perpendicular from the electrode surface to the ion in solution.



Helmholtz double layer of width *a* / 2, where *a* is the diameter of the solvated counter ion

Helmholtz Double Layer

Assumption:

The negative ions are considered point charges so that the charge density, ρ, **in the region between the positively charged electrode surface (at x=0) and the Helmholtz plane (at $x = a/2$)** is zero

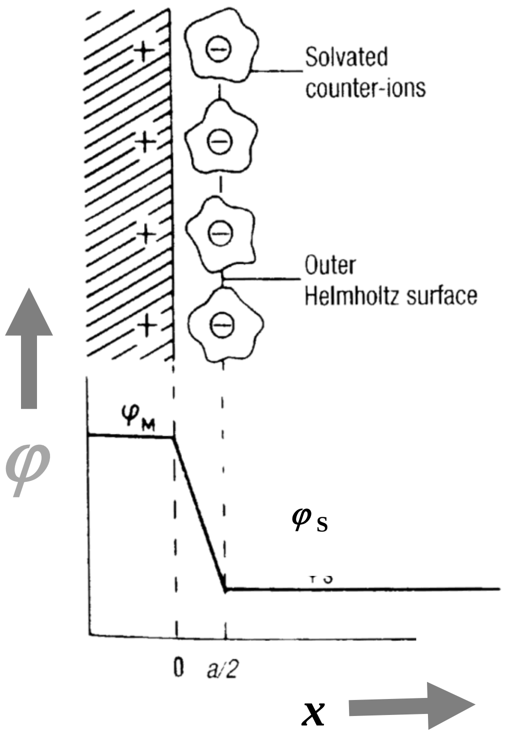
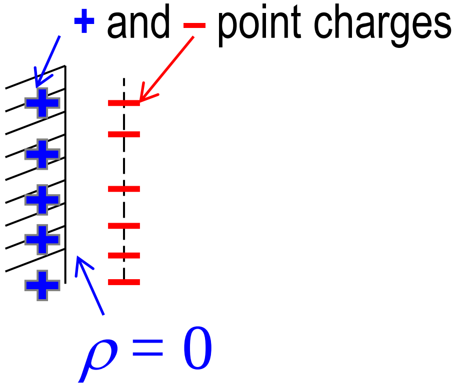


Fig 3.15. Potential distribution between electrode and outer Helmholtz surface

This situation is described by the simple eqn. 3.131



$$\frac{d^2\varphi}{dx^2} = 0 \qquad \text{Eqn. 3.131}$$

Now integrating eqn. 3.131 twice from 0 ≤ x ≤ a/2 gives eqn. 1.132:

$$\varphi = \varphi_M - \frac{2(\varphi_M - \varphi_S)x}{a} \qquad \text{Eqn. 3.132}$$

Which is a simple mathematical model of the potential from the electrode into solution

Conclusions:

- **Helmholtz model straightforwardly predicts the potential drop from φ_M to φ_S but is incomplete.**
- **Helmholtz model *takes no account of the thermal motion* of the ions.**
- **The thermal motions tend to loosen ions from the compact layer.**

Diffuse Double Layer **…** the Gouy-Chapman Model

Gouy and Chapman’s view:

The double layer consists of ions in a constant thermal motion in a spatially quite extended region near the electrode surface (diffuse double layer) *with no compact inner layer*.

Mathematical Description:

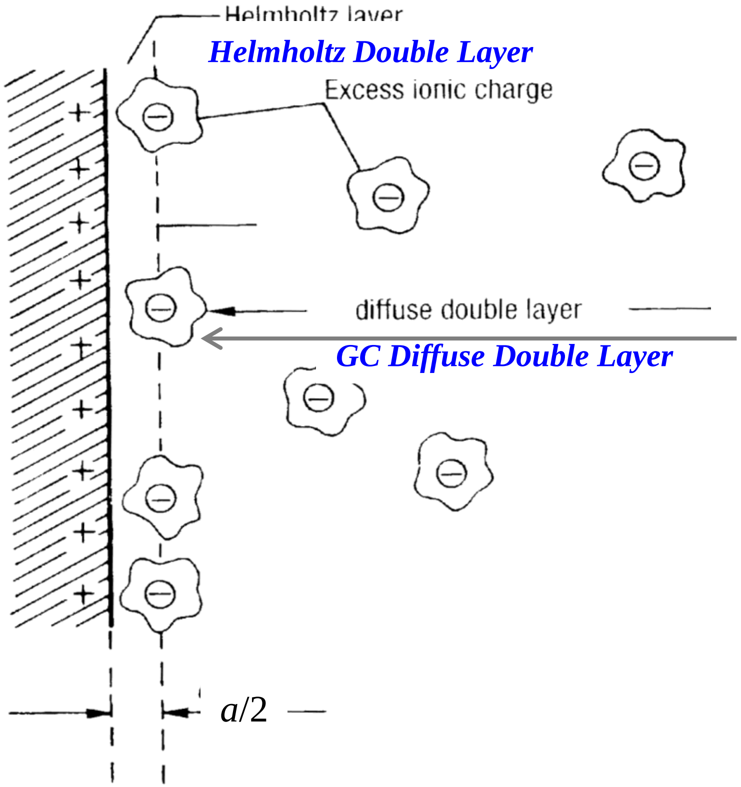
If n_i^0 is the number of ions of type i per unit volume present in the bulk of the electrolyte at thermal equilibrium, then applying the Boltzman factor, we get that n_i at x is:

$$n_i = n_i^0 \exp\left[\frac{-z_i e_0 \varphi(x)}{k_B T}\right]$$

Stern double layer model

n_i is the number of ions I per unit volume and n_i^0 is the number of ions I per unit volume of bulk electrolyte

Let introduce $\xi = x-(a/2)$ and realize that far into the bulk of the electrolyte, where $\varphi(x) \rightarrow \varphi s$ we will find $n_i \rightarrow n_i^0$ which leads to the distribution of ions as given by equation 3.134



Helmholtz and Gouy-Chapman double layers

$$n_i = n_i^0 \exp\left[-z_i\, e_o \left(\varphi(\xi) - \varphi_S \right) / k_B T \right]$$ Eqn. 3.134

If we introduce a constant *k* that is proportional to the ionic strength, *I*, the Poisson Equation can be written f

$$\frac{d^2\varphi}{d\xi^2} = \kappa^2(\varphi(\xi) - \varphi_S)$$

which solves to give

$$\varphi(\xi) - \varphi_S = \mathrm{const}\cdot e^{-\kappa\xi}$$

limiting condition:

At **ξ = 0** or ***x* = *a*/2** the potential is that present at the outer Helmholtz plane , φ_{OHP}.

$$\varphi(\xi) - \varphi_S = (\varphi_{OHP} - \varphi_S)e^{-\kappa\xi}$$ Eqn. 3.139

The total Galvani potential drop Δ*φ* between the interior of the electrode and the interior of the solution is now divided in 2 parts (**as derived by Stern**) :

Helmholtz **GC - diffuse layer**

$$\Delta\varphi = \underbrace{(\varphi_M - \varphi_{OHP})}_{\text{Helmholtz}} + \underbrace{(\varphi_{OHP} - \varphi_S)}_{\text{GC - diffuse layer}} = \Delta\varphi_H + \Delta\varphi_{diff}$$ Eqn. 3.140

where 1) $\Delta\varphi_H$ is the compact double layer (Helmholtz) term

and 2) $\Delta\varphi_{diff}$ is the diffuse (Gouy-Chapman) term.

$$\Delta\varphi = (\varphi_M - \varphi_{OHP}) + (\varphi_{OHP} - \varphi_S) = \Delta\varphi_H + \Delta\varphi_{diff}$$

Stern's Model

Analyzing Potential Profile:

$\Delta\varphi_H$ is the potential drop across the Helmholtz layer and $\Delta\varphi_{diff}$ the potential drop across the diffuse double layer; this latter potential drop is known as the **zeta potential**, ζ, so … $\Delta\varphi = \Delta\varphi_H + \Delta\varphi_{diff} = \Delta\varphi_H + \zeta$.

The distance $\xi = 1/k$, from the outer Hernholtz plane to the point at which the diffuse-layer potential has dropped to a value $1/e$ of its total change from OHP to bulk solution is a measure of the thickness of the double layer.

- **Charge Profile**

The charge of the double layer σ^M could be shown to depend on ζ in the following way:

$$Q = 11.7C^{*1/2}\sinh(19.5z\,\zeta)$$

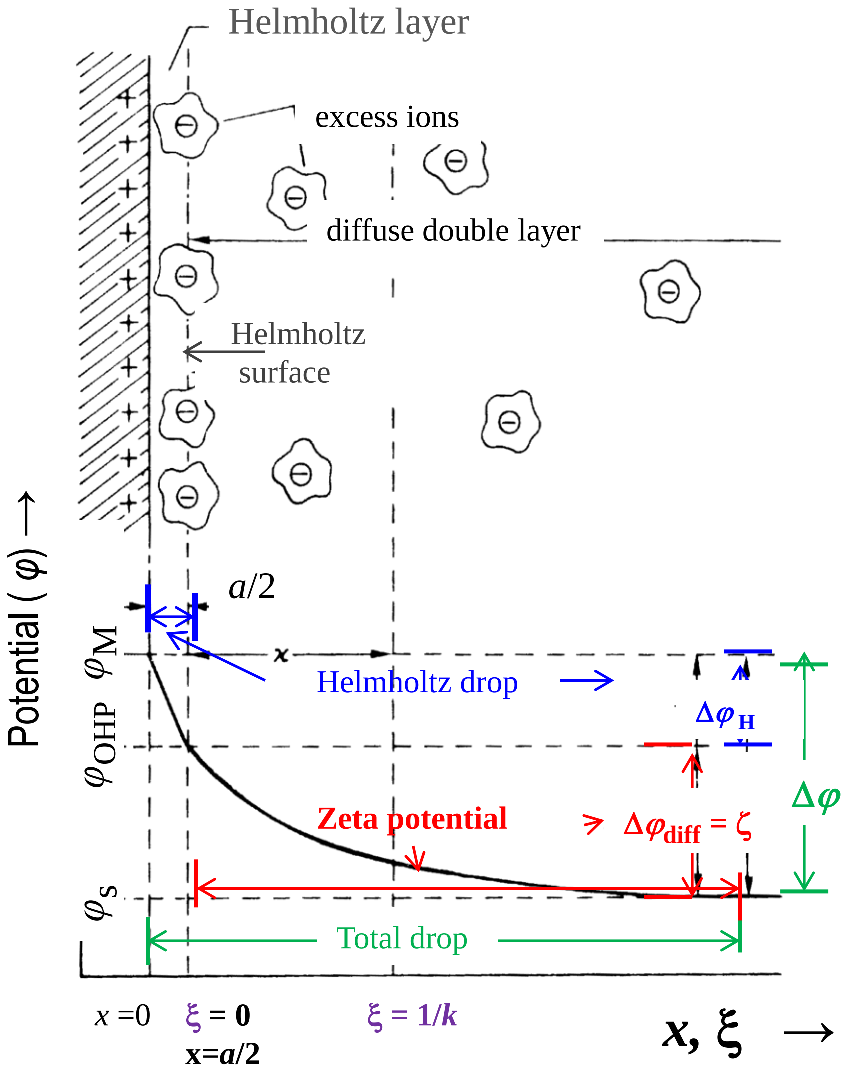
- **Differential Capacitance:**

The differential capacitance $C_d = dQ/d\zeta$ could be shown to follow the dependence,

$$C_d = 228zC^{*1/2}\cosh(19.5z\,\zeta)$$

Mathematically Stern Combines Helmhotz's model and Gouy-Chapman's (diffuse double layer) model to get finally:

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}$$



Potential distribution at the Stern's double layer

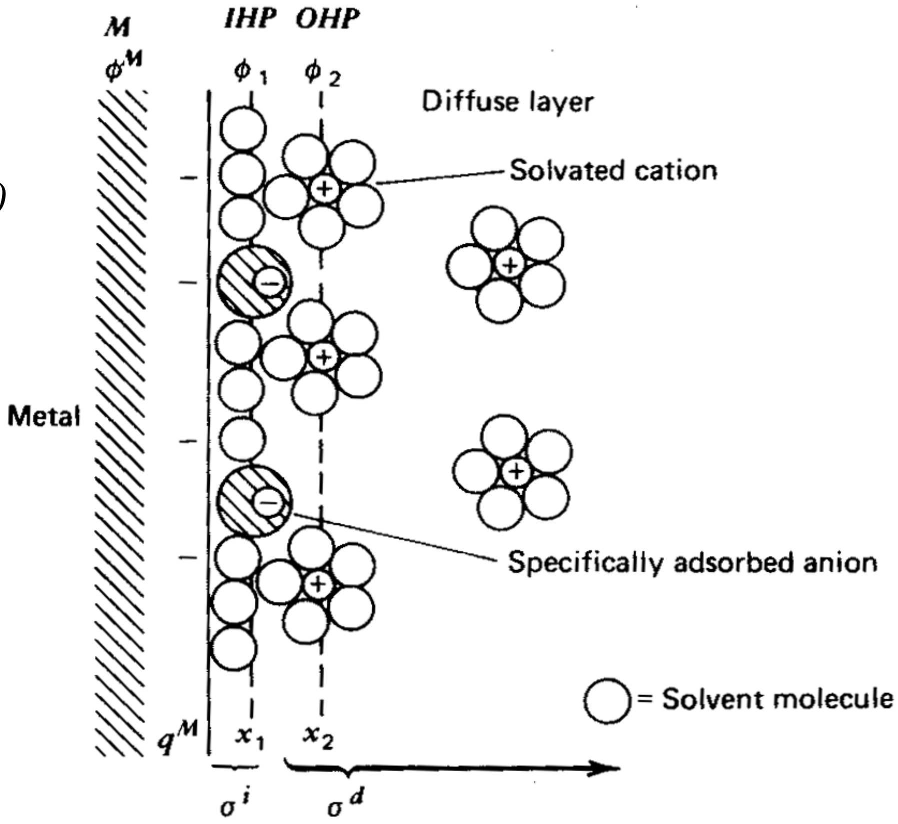
Stern's Model *plus the adsorption of ions* in the Double Layer Field

Stern's model with adsorption:

- Helmholtz Compact layer
  - Inner Helmholtz layer (*Specifically adsorbed ions, molecules, etc.*)
  - Outer Helmholtz layer (*Nonspecifically adsorbed ions)*
- Diffuse layer (*All ions*)

Potential of Zero Charge – no adsorption

- φ_{pzc} is the potential of zero charge.
- φ_{pzc} is the inner potential of an electrode on whose surface there are no free excess charges (either adsorbed on or in the diffuse layer).
- φ_{pzc} is not equal to φ_{S} (the solution potential) due to presence of solvent dipoles on the electrode surface which gives rise to a potential drop
- E_{pzc} is the potential of an electrode (versus a reference) on whose surface there are no free excess charges (either adsorbed on or in the diffuse layer).

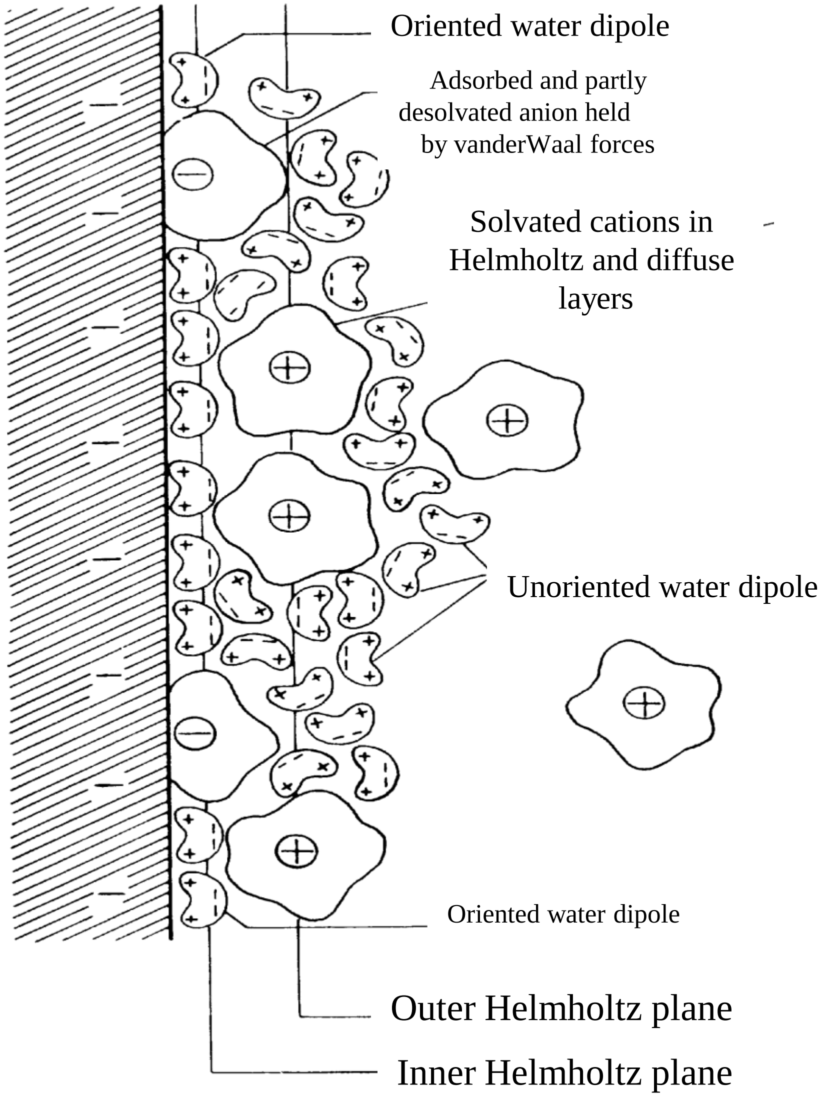


Refined view of the double layer

Summary of the Double Layer with the Adsorption of Ions, Dipoles and Neutral Molecules

Summary of today's view of the double layer structure:

- **Inner Helmholtz plane:** Could contain only specifically adsorbed ions - ions with partially stripped solvent sheath;
- **Outer Helmholtz plane:** Contains ions with complete solvent sheaths. These ions are attracted toward the electrode only by electrostatic forces;
- **Diffuse part of the double layer:** Described by Gouy-Chapman approach.
- **PZC** **-** The potential of an electrode on whose surface there are no free excess charges, either specifically adsorbed ions or excess ions of either charge in the diffuse double layer, is termed its ***potential of zero charge***, φ_{pzc}.
    - In general, the value of φ_{pzc} is not identical to φ_s, the potential in the interior of the electrolyte, owing to the presence of solvent dipoles at the surface, which give rise to an unknown additional potential drop



Molecular Structure of the Double Layer

The Double-Layer Capacity

The electrolytic double layer can be considered most simply as a parallel plate capacitor and:

$$Q = C\,\Delta\varphi$$

and since $\Delta\varphi - \Delta\,\varphi_{pzc} = E - E_{pzc}$, we have

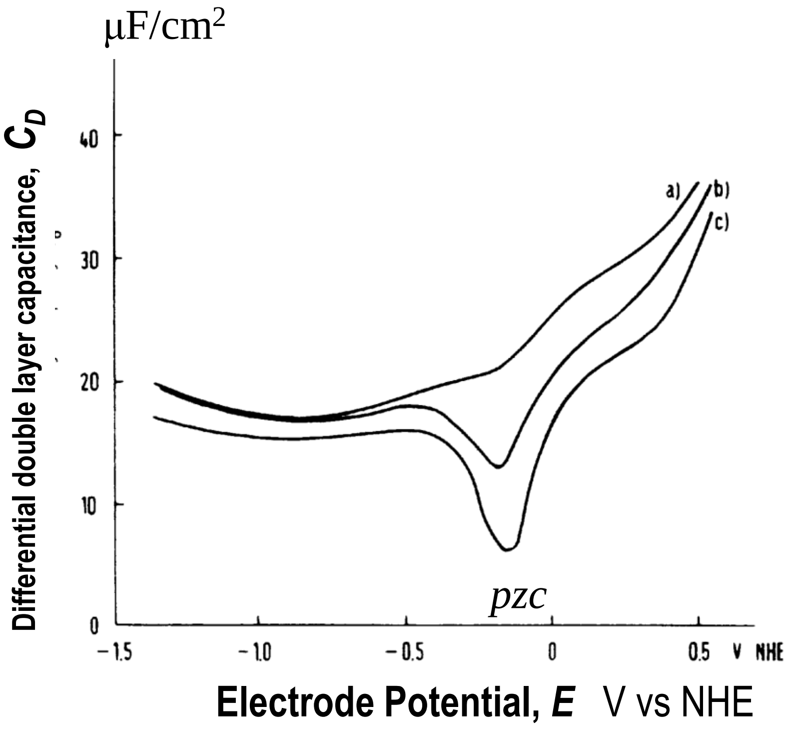
$$Q = C(E - E_{pzc})$$

which insures $Q = 0$ at the point of zero charge

- Parallel-plate capacitor will be most apt where the double layer is most closely described by the Helmholtz model, i. e. at higher concentrations of electrolyte.

- At lower concentrations the diffuse part will also contribute and:

$$C_d = \frac{dQ}{dE}$$



Differential double-layer capacity C_d at mercury at 25 'C in non adsorbing NaF solution of concentrations:

(a) 0.1 M;
(b) 0.01 M;
(c) 0.001 M.

This way, measuring the current needed to charge or discharge the double layer we get information for C_d according to:

$$I_C = \underline{\frac{dQ(E)}{dt}} = \frac{dQ}{dE} \cdot \frac{dE}{dt} = \underline{C_d \cdot \frac{dE}{dt}}$$

Potential Profiles on Specific Adsorption of Ions

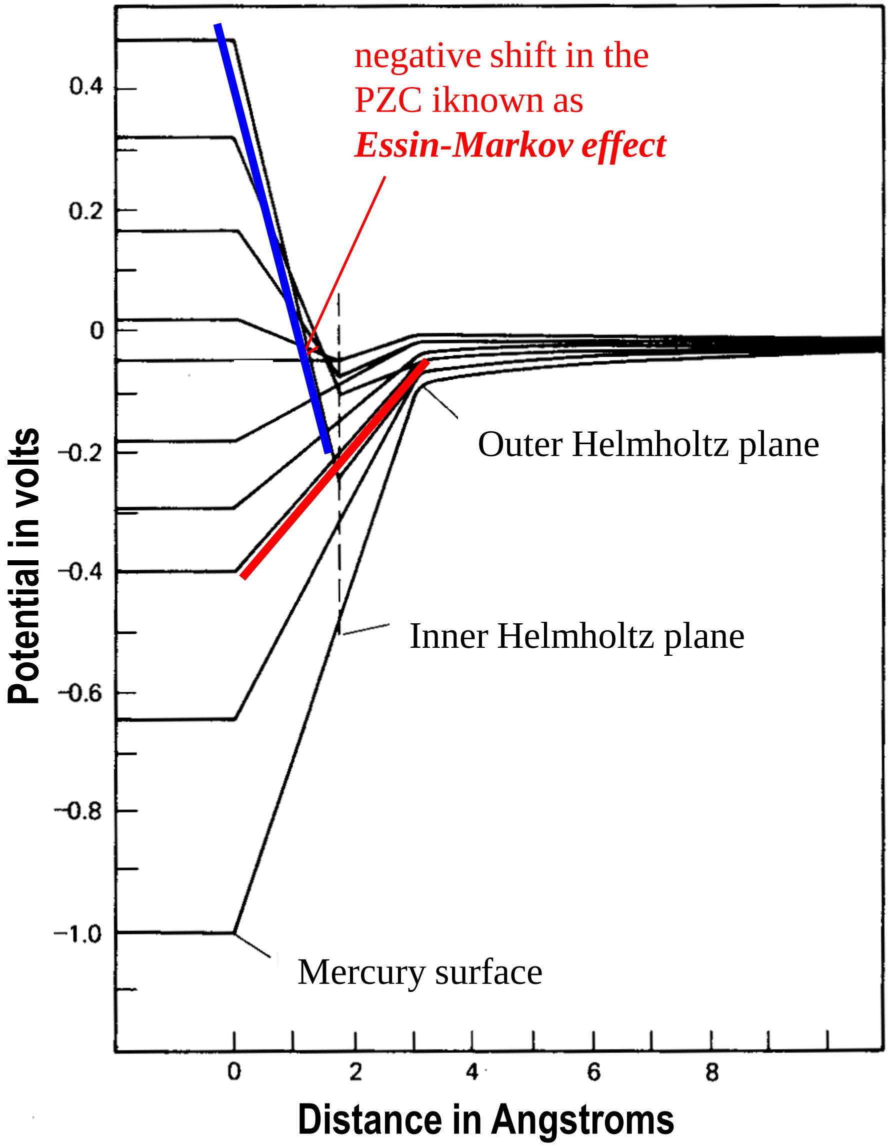
The specific adsorption of ions, (e.g. Cl^- on Hg) at the electrode surface is driven by specific interactions which are short-range in nature. The GouyChapmanStern model does not take into account any specific interactions.

In such a case, there is an amount of adsorbed anions at potentials negative to the PZC!

The forces responsible for specific adsorption are strong enough to withstand the opposing Coulombic field in at least part of the negative region. As a result, the minimum in the C-E curve shifts in negative direction.

The negative shift in the PZC is known as ***Essin-Markov effect.*** The extent in that shift depends mostly on the strength of the specific adsorption.

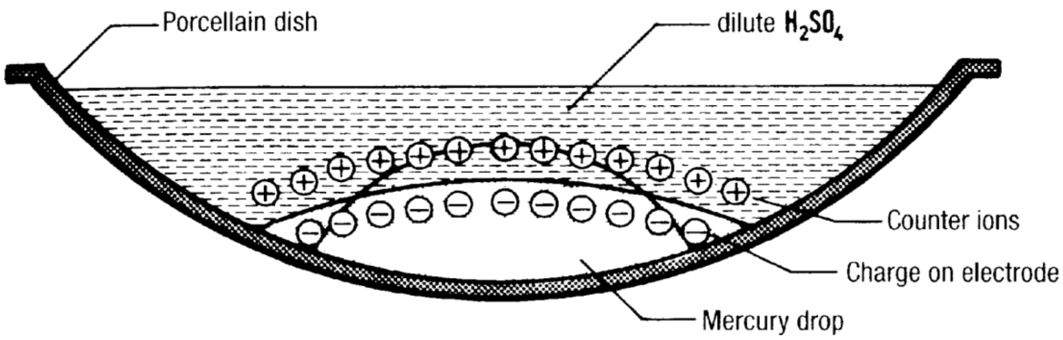
Finally, *specifically adsorbed layers of ions could alter the potential profiles in the interfacial zone to an extreme degree.* Note in the figure particularly the traces for the most positive potentials (sharper slope for blue versus red line at same magnitude of potential).



negative shift in the PZC iknown as ***Essin-Markov effect***

Potential profiles in the double layer for Hg in contact with 0.3 M NaCl. Potentials given with respect to PZC in non-adsorbing NaF

Electrocapillary p126

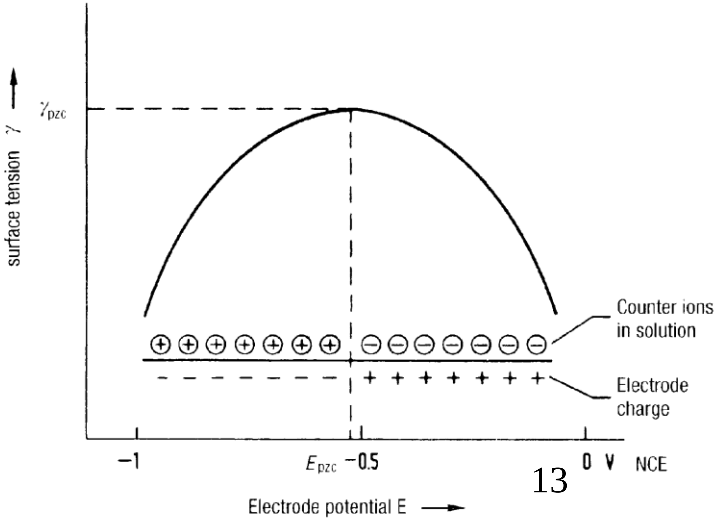


Flattening of the surface of mercury on formation of an electrolytic double layer, represented for negative charging of the metal with respect to the solution.

Electrical charges of the same sign within a space-charge layer will repel one another, and at the electrode surface will tend to extend the surface as far as possible. The resultant repulsion between the ions leads to a flattening a mercury droplet as shown in Figure

At the PZC we anticipate minimum in the repulsion and maximum in the surface tension, respectively.
At that potential *the droplet will be most curved*.

The surface tension, γ, dependence on the electrode potential is known as ***electrocapillary curve***.



The Lipmann Equation p126

The electrocapillarity curve can be treated quantitatively.
For a surface with a charge density σ, a small change in the potential dE results in a work for opening of a new area ($q_M\,dE$) which is offset by the change in the free energy per unit area, dγ:

$$\sigma dE + d\gamma = 0 \qquad \text{or} \qquad \frac{d\gamma}{dE} = \sigma$$

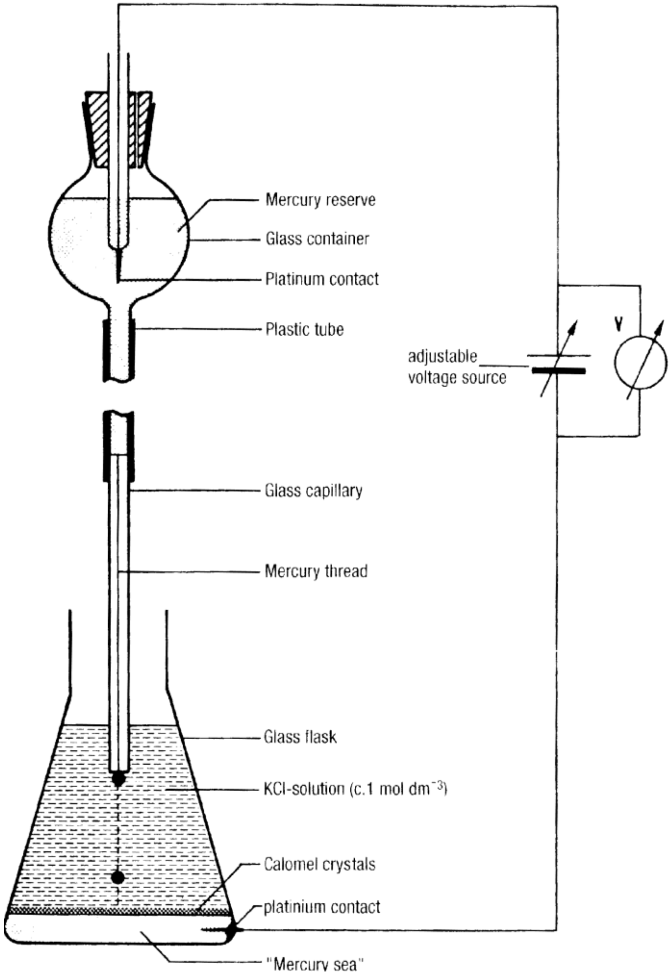
given that $\sigma = C(E - E_{pzc})$, where C is the integral capacitance per unit area, we can integrate equation) assuming C to be constant, and we obtain finally:

$$\gamma_{pzc} - \gamma = -\frac{C(E - E_{pzc})}{2}$$

Differentiation of the Lippmann equation with respect to potential leads to:

$$\frac{d^2\gamma}{dE^2} = \frac{d\sigma}{dE} = -C^d$$

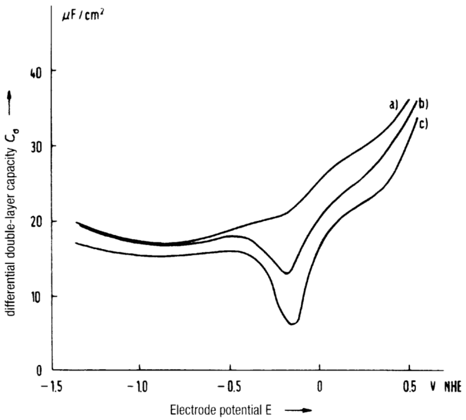
The differential capacitance, C^d, can be obtained from a plot of surface tension, γ, versus electrode potential, E



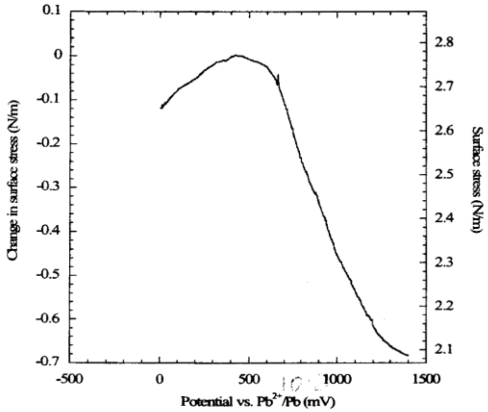
Dropping mercury electrode

Alternative Methods for Determining the PZC p123

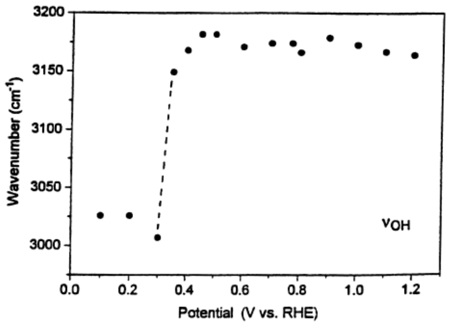
- ***Impedance methods*** (Differential Capacitance): According to the Lipmann equation C_d should display minimum at PZC. By impedance means one can monitor C_d as a function of E. Impedance methods are the best for studying solid electrodes.



- Methods based on the ***mechanical properties*** (Surface Stress): Small alterations in potential lead to changes in surface tension and hence to small changes in surface stress. The strain associated with this change in stress can be picked up by cementing the electrode, in the form of a thin layer. The surface stress should display maximum at PZC.



- Methods based on ***direct investigation of the electrolyte*** part of the double layer (Fourier Transformed IR Spectroscopy - FTIR). Here the orientation of water molecule could be monitored. At PZC this orientation changes.

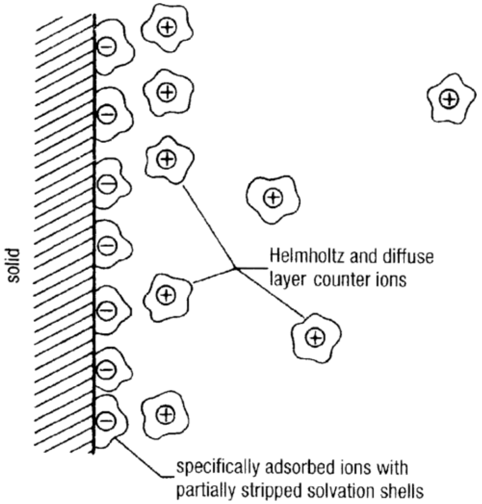


Electrokinetic Effects: Electro- phoresis, osmosis and their reverse effects p116

Electrolytic double layers can form at solid-liquid phase boundaries even if the solid concerned is not an electronic Conductor, e.g.,

- Specific adsorption of ions on dielectric surfaces
- or selectively permeable membranes can serve as a charge carrier

for double layer formation.

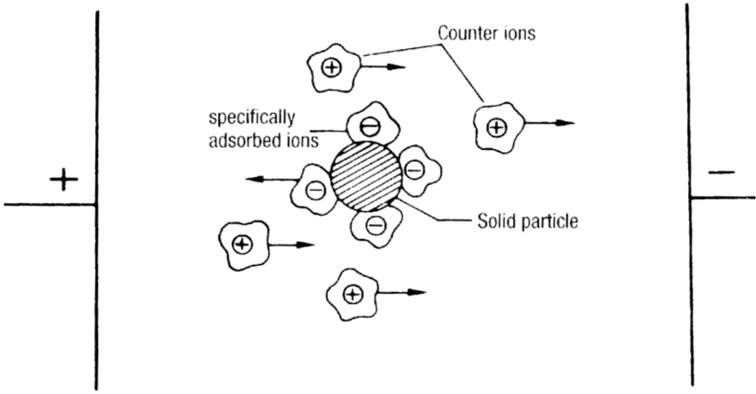


Formation of an electrolytic double layer through specific adsorption of ions

Electrophoresis:

Electric potential moves charges.

Suspended solid particles or colloidally dispersed material may be treated in the same way. In such a case the large charge to particle mass ratio serves as a base for the so-called electrophoresis - migration of charged particles in electric field. Most frequently, the colloid particles migrate toward the positive electrode.



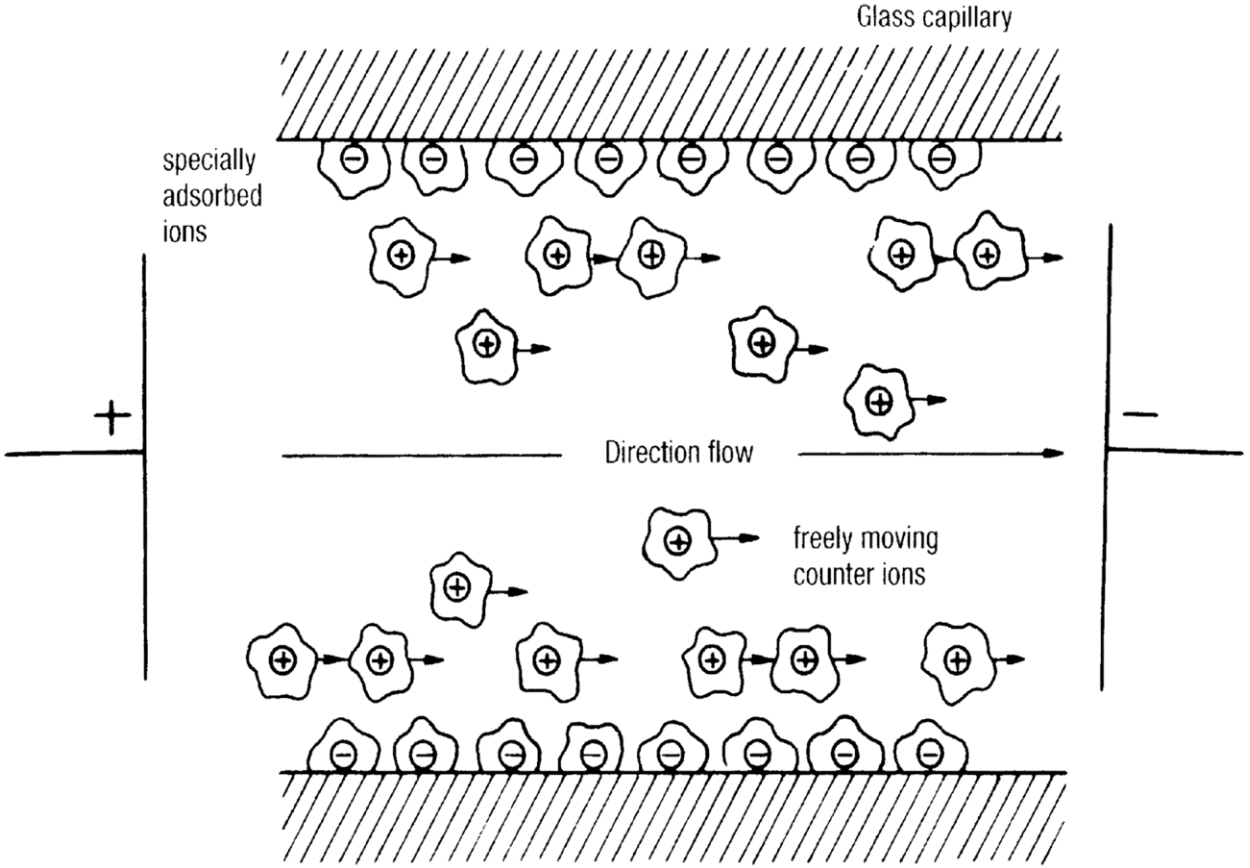
Electrophoresis – migration of charge in electric field

Dorn effect – reverse of electrophoresis:

Moving charges create electric potential

If the colloidal particles undergo *forced movement* through an electrolyte solution, for example by the imposition of ultrasonic vibrations, then a *potential difference is observed in the direction of motion*.

Electro-osmotic current



Electro-osmosis: p130

When an electric field is applied along a fixed charged solid surface, the counter ions in the diffuse layer can move with the field, whereas the ions adsorbed on the surface cannot. The result is an ion current along the surface. If the process takes place through a porous solid this effect results in *an osmotic pressure buildup*. This effect is termed the ***electro-osmotic effect***.

Streaming potential – reverse of electro-osmosis:

If a *stream of ions is forced through a capillary or a porous electrode*, which *gives rise to a potential* difference termed ***streaming potential.***

Next: Applications of Potential Difference